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COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT

LEIDEN.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

VOLUME XIII.

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COMMUNICATIONS

FROM THE

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BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 133ª.

H. KAMERLINGH ONNES. Further experiments with liquid helium. H. On the electrical resistance of pure metals etc. VII. The potential difference necessary for the electric current through mercury below 4°.19 K.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **22 Februari 1913**, p. 1284—1302.)

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H. KAMERLINGH ONNES. *Further experiments with liquid helium.* H. *On the electrical resistance of pure metals etc.* VII. *The potential difference necessary for the electric current through mercury below* 4°.19 K.

§ 1. *Difficulties involved in the investigation of the galvanic phenomena below* 4°.19 K. In a previous Communication (No. 124*c* of Nov. 1911) we related that special phenomena appeared when an electric current of great density was passed through a mercury thread at a temperature below 4°.19 K., as was done to establish a higher limit at every temperature for the possible residual value of the resistance. Not until the experiments had been repeated many times with different mercury threads, which were provided with different leads chosen so as to exclude any possible disturbances, could we obtain a survey of these phenomena. They consist principally herein, that at every temperature below 4°.18 K. for a mercury thread inclosed in a glass capillary tube a "*threshold value*" of the current density can be given, such that at the crossing of the "threshold value" the phenomena change. At current density below the "threshold value" the electricity goes through without any perceptable potential difference at the extremities of the thread being necessary. It appears therefore that the thread has no resistance, and for the residual resistance which it might possess, a higher limit can be given determined by the smallest potential difference which could be established in the experiments (here $0.03 \cdot 10^{-6}$ V) and the "threshold value" of the current. At a lower temperature the threshold value becomes higher and thus the highest limit for the possible residual resistance can be pushed further back. As soon as the current density rises above the "*threshold value*", a potential difference appears which *increases more rapidly than the current*; this seemed at first to be about proportional to the square of the excess value of the current above the initial

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value, but as a matter of fact at smaller excess values it increases less and at greater excess values much more rapidly.

It appears that the phenomena at least for the greater part are due to a heating of the conductor. It has still to be settled whether this heating is connected with peculiarities in the movement of electricity through mercury, which for a moment I thought most probable in connection with various theoretical suppositions (comp. § 4), when this metal has assumed its exceedingly large conductivity at low helium temperatures; or whether it can be explained by the ordinary notions of resistance and rise of temperature of a conductor carrying a current, perhaps with the introduction of extra numerical values for the quantities that influence the problem. A further investigation of this with mercury in the most obvious directions, such as cooling the resistance itself with helium, presents such difficulties that I have not pursued it, as it would not be possible to prepare the necessary mercury resistances by the comparatively simple process of freezing mercury in capillary tubes. When I found (Dec. 1912) that, as I shall explain in a following Comm., (see VIII of this series, Comm. N^0. 132*d*) tin and lead show similar properties to mercury, the investigations were continued with these two metals. Thus the experiments with mercury which are described below may be regarded as a first complete series.

Various circumstances combined to make even the investigation of the mercury inclosed in capillary tubes difficult. A day of experiments with liquid helium requires a great deal of preparation, and when the experiments treated of here were made, before the latest improvements in the helium circulation were introduced, there were only a few hours available for the actual experiments. To be able to make accurate measurements with the liquid helium then, it is necessary to draw up a programme beforehand and to follow it quickly and methodically on the day of experiment. Modifications of the experiments in connection with what one observes, must usually be postponed to another day on which experiments with liquid helium could be made. Very likely in consequence of some delay caused by the careful and difficult preparation of the resistances, the helium apparatus would have been taken into use for something else. And when we could go on with the experiment again, the resistance sometimes became useless (e. g. § 3) because in the freezing the fine mercury

Errata Communication N⁰. 133.

p. 4 line 20 from the top: for 132*d* read 133*d*.

thread separated, and all our preparations were labour thrown away. Under these circumstances the detection and elimination of the causes of unexpected and misleading disturbances took up a great deal of time.

§ 2. *Confirmation of the sudden disappearance of the resistance at* 4°.19 K. *and first observations concerning the potential phenomena at low temperature.* The first experiments which showed the phenomena to be discussed were made in October 1911, with the resistance described in the previous Comm. (No. 124*c*).

α. Before discussing them let us consider for a moment the measurements which were made with this resistance at 4°.23 K. and add something to what we said about them in the previous Comm.[1]). In the measurements which we are considering we could take advantage[2]) of the presence of Hg_5 to measure the portions between Hg_1 and Hg_5 and between Hg_5 and Hg_4 separately and afterwards the two in series. The result was $Hg_1Hg_5 = 0.0518\ \Omega$, $Hg_5Hg_4 = 0.0617\ \Omega$, together $0.1135\ \Omega$. This gave a necessary check on the determination of both in series $Hg_1Hg_4 = 0.1142\ \Omega$[3]). These values, considering that they belong to about 65 Ω (calculated for solid mercury at 0° C.) correspond pretty well to the results obtained in the experiments in May 1911 Comm. No. 122*b*, July 1911, viz. that a resistance of about 40 Ω (calculated for solid mercury at 0° C.) becomes 0.084 Ω at the boiling point 4°.25 K.

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[1]) For a survey of the observations concerning mercury at the lowest temp. in three figs. with rising scale the reader is referred to Rapport du Comité Solvay, Nov. 1911, fig. 11, 12 and 13 (in which read 13 for 12, and 12 for 13), Leiden Comm. Suppl. N⁰. 29.

[2]) The measurements with a view to which the tube Hg_5 was added (see Plate I in Comm. No. 124*c*) were not made then, but postponed till later. (See § 5). They were to enable us to judge of the dependence on the section.

[3]) The resistance at the boiling point of hydrogen was 3.27 Ω. A further Comm. will refer to the difference of the ratio of the values at 273° K. and 20° K. to those in previous measurements, which is here of no consequence and is due to different ways in which the mercury freezes. In the experiments described here similar differences were constantly found.

It should be mentioned that the glass was tested at all temperatures for its insulation and also that when the potential difference at the terminals was found to be zero, it was always ascertained that the resistance of the galvanometer circuit which served to measure the P. D. had not changed materially.

β. In these experiments the validity of Ohm's law was confirmed above the point where the almost sudden disappearance of the resistance begins which was treated of in the previous Comm. by one measurement at a current strength of 3 and another of 6 milliampères which within the limits of accuracy gave the same result (0.0837 at 3, and 0.0842 at 6 m.A.). In connection with the experiments in Comm. No. 122*b* July 1911 we may mention that they were made with a resistance of a different kind to that [1]) which was used for the experiments in Oct. 1911, viz. the one which appears in the Plate of Comm. No. 123 as Ω_{Hg} (of about 40 Ω calculated for solid mercury at 0° C.). Narrow tubes alternately going up and down were connected by expansion heads (as in the Plate in Comm. No. 124*b*) and connected to platinum leading wires by fork shaped turned down wide pieces [2]), which can be seen distinctly on magnification on the Plate in Comm. No. 123 (where the resistance is shown in the cryostat).

γ. After this digression about the change in the resistance between ordinary temperature and the boiling point of helium, let us return to the experiments in and below the region of the sudden fall of resistance, which as has been said at the beginning of this § were made with a mercury resistance with mercury leads, and which were treated of in § 3 and fig. 1 of the previous Comm. (Dec. 1911) about the resistance at helium temperatures (experiments of Oct. 1911).

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[1]) This was a ramification of solid mercury threads consisting of a U divided at both ends, allowing measurements as well by the method of Callendar as by the potentiometer method.

[2]) In the resistances which were used for the first experiments with mercury, the platinum leading in wires were simply sealed into the wider portions of the resistance tube at the ends (the expansion heads). When the mercury cannot be poured into the tube in vacuo but has to be boiled in the tubes in order that they may afterwards be exhausted without any chance of the mercury separating there is some fear of platinum amalgam being formed which might penetrate into the current circuit. In order to prevent this the wide ends of the tubes are according to a suggestion of Mr. G. Holst, made fork shaped the prongs which contain the sealing place being turned down. In this manner mercury leads may in general be replaced by platinum leads without any trouble being experienced with regard to the resistance of the current circuit. By a comparison with experiments with mercury leads it had been found that the mercury-platinum contacts could be allowed in the potential circuit.

At 4°.20 K. we find ourselves in the higher part of the almost sudden change. In the case that we are now about to treat it had almost become complete. With a current of 7.1 m.A. it was a considerable time before the condition became stable. When this had taken place, the resistance of Hg_1Hg_4 was found to be 0.000746 Ω [1]).

At a further cooling of the mercury to $4°.19^5$ K. with the same strength of current the result was only $Hg_1Hg_4 < 1.4.10^{-5}\ \Omega$.

δ. At 4°.19 K. we come into the lower part of the region with which this Comm. deals in particular. The strength of the current had to be increased to 14 m.A. to give a perceptable potential difference at the ends of the resistance but even then it remained doubtful. It became distinct at a current strength of 0.02 amp. and was then $2.5.10^{-6}$ V. At 0.023 amp. it became 5.10^{-6} V, and at 0.0288 amp. 16.10^{-6} V.

When the mercury thread was cooled by helium which evaporated at a mercury pressure of 40 cm. that is at about 3°.65 K., with a strength of current of 0.49 amp. there was no potential difference to be observed at the extremities, the current had to be increased to the threshold value of 0.72 amp. to make the potential difference observable.

ε. The highest limit of the value which the residual resistance can have in the case of the lowest temperature, is therefore in these last experiments again considerably reduced by the application of stronger currents, viz. in this case (3°.65 K.) to 10^{-9} of the resistance at 0° C. (calculated for solid mercury) while in Comm. No. 122*b* June 1911 at 3° K. it could only be put at $< 10^{-7}$.

§ 3. *Appearance of the same potential phenomena in a revised arrangement of the experiment.* The appearance of the peculiar phenomena immediately above the "threshold value" of the current, gave rise to the question whether the just established limit would not have to be put lower when it should be possible to avoid the disturbances, which might still exist, and perhaps showed themselves in the above mentioned phenomena. The most obvious thing in the first place was to prevent the possibility with great current density of heat, developed in places in the main circuit where the temperature is higher, penetrating to the resistance that is being measured. By this, from both ends, the thread would be brought over part of its length above the vanishing temperature, which would immediately cause considerable potential differences. In this connection we thought particularly of JOULE heat. PELTIER heat, which we had noticed before (Comm. No. 124*c*) but which for the present we attributed to impurities in the mercury in the legs, and assumed to be present only in the neighbourhood of the transition from solid to liquid, I took to be as far as possible excluded by the fact that the whole current system was of pure solid mercury at the very low temperatures. Now this belief may be untrue, because owing either to tension caused by a difference of expansion to that of glass which it seems can be fairly great as the mercury sticks to the glass, or through the contact between crystals of different kind or size, even in the purest mercury considerable thermopowers may possibly appear. But then they have their seat, as shown by the previous experiments, chiefly in places above the temperature of liquid air and PELTIER heat in these places need not be feared. To avoid disturbances of the sort to which we referred the experiment

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[1]) Here and in the following we speak repeatedly of resistance, without wishing to give it beforehand any other meaning than: calculated by Ohm's law from the strength of current and the pressure difference observed.

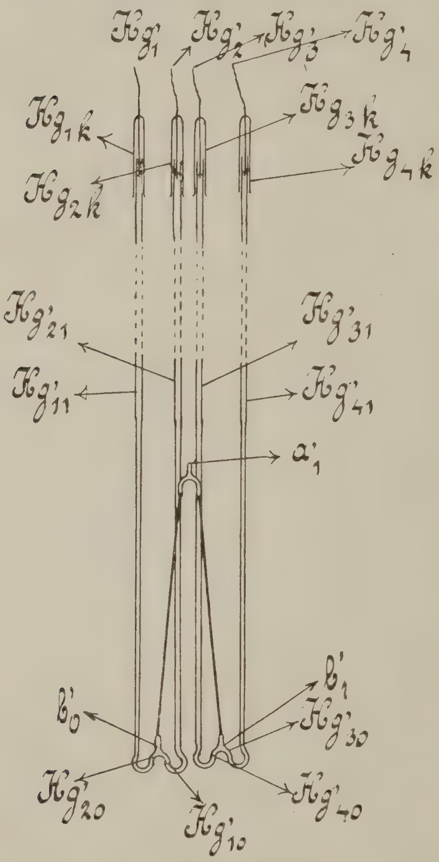

Fig. 2.

was repeated with resistances of such a kind that the conduction of any kind of heat from a part of the apparatus where there was higher temperature was made very difficult. The accompanying figure, which should be compared with figs. 1 and 2 on the Plate in the previous Comm. N⁰. 124*c*. (VI of this series) shows the form chosen. The mercury threads which lead the current to and from the apparatus, run first through the liquid helium downwards, before they come out into the widened parts of the resistance. The potential wires do the same [1]). Close to the surface of the liquid the leading wires can be thin on account of the low temperature. There were two resistances of the same kind in the cryostat, one of 50 Ω and the other of 130 Ω, the section of the tubes was about 0.004 mm^2 and 0.0015 mm^2. They were intended to investigate the influence of the section of the tubes upon the phenomena examined, a thing thad had been aimed at already before (see § 2) but did not succeed and the preparation of the narrowest one in particular had given great difficulties. It gave way during the experiment, so that the question of the influence of the section had again to be solved later on (see § 5). The experiments which were of chief importance for the matter under consideration were made in Dec. 1911 with the smallest of the two resistances, the section of the narrow resistance tube was here a little smaller than the mean in the resistance which was used for the experiments in Comm. No. 124*c*.

On the whole the results were the same as by previous measurements. Although great care [2]) was again given to the distillation of the mercury with the help of liquid air [1]), the mercury legs, as has been observed, gave considerable thermo-power; the legs with the smallest thermo-power were chosen as potential wires [2]).

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[1]) Corresponding parts are indicated by the same letters, modified parts by the addition of an accent. A small additional improvement was further introduced into the contacts at the upper end, the four leading tubes were simply left open (which made it easy to add mercury which the contraction during the freezing made necessary), and bell shaped tubes Hg_k were placed over the extremities in which the platinum wires Hg' etc. are sealed which connect the resistance to the current sources and the measuring apparatus. Platinum amalgam (see note 2. p. 6) need not be feared in this case, so that the complication of the inverted forks was superfluous.

We do not need here to enter into particulars of precautions such as the protection of contacts against changes of temperature, and others which have reference to the special circumstances under which the resistance measurements were made.

[2]) In § 9 it in demonstrated that in repeating the experiments less precautions would have been sufficient.

There was some indication that the resistance of the mercury in narrower tubes falls a trifle less than in wider ones, when the tubes are cooled to 4°.25 K. (boiling point of helium). The new experiments also raised the question whether the almost sudden changes were found at a slightly different temperature of the bath in the narrower than in the wider tubes. But all this concerns particulars which can probably be explained by differences of crystallization and of heating by the current.

That the almost sudden change begins at 4°.21 K. [3]) and ends within a fall of 0°.02, was again confirmed with a resistance of about 50 Ω (calculated for liquid mercury at 0° C.).

Concerning the threshold value of current and the potential differences appearing at higher currents, i.e. the phenomenon to which the investigations were especially directed this time (Dec. 1911) results were obtained which correspond pretty well with the previous ones (Oct. 1911) if we assume that the origin of the phenomenon is in the resistance itself, and at the same time make the natural assumption that the potential difference increases with the current density, and

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[1]) In the distillation the mercury was not heated above 65° and 70° C. while the cooling was done with liquid air. In order not to have to wait too long to procure a sufficient quantity it was done in an apparatus shown in fig. 2 at $^{1}/_{3}$ of the actual size. The mercury is brought into the double walled tube *a b* (with the reception beaker *c*), which was sealed off below at *e*. It is exhausted through tube *d*, while the mercury is warmed and then sealed off at *f*.

The lowest part is immersed in warm water; in the hollow *a* liquid air is poured. In 3 hours about 2 cm^3. goes over; the condensed mercury in *c*, is afterwards poured out at *f*.

[2]) It amounted to only 12 microvolts, and this was compensated. The seat of these E.M.F. (up to 340) is to be found principally in the portion above hydrogen temperature.

[3]) This means more precisely 0°.04 below the boiling point of helium.

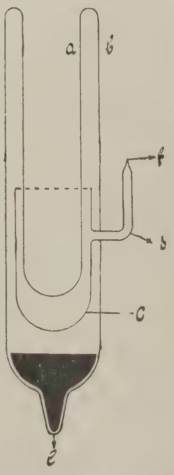

Fig. 2.

with conductors joined in series is equal to the sum of the potential differences in each of these conductors. This is shown in the table, in which both series of observations are combined, and holds both for the minimum value of the current at which the potential difference appears, and the value of the potential difference at a given excess value of current and a given temperature.

TABLE I.

Potential difference of the extremities of mercury threads carrying a current.

Temperature.	Current density in ampères per mm^2.		Potential difference in microvolts.	
	October 1911.	December 1911.	October 1911 $l = 7 \times 20$ cm.	December 1911 $l = 20$ cm.
3°.65 K.	0.49 × 190		0	
		0.510 × 260		0
	0.56		0	
		0.665		0.5
	0.72		7 × 1.14	
		0.890		4.7
		1.10		12.7
4°.19 K.	0.010		0	0
	0.014		7 × 0.017	
		0.016		0.4
	0.020		7 × 0.36	
	0.023		7 × 0.71	
		0.024		4.7
	0.028		7 × 2.3	

For we must remember that the previous resistance consisted of 7 U-shaped tubes not all precisely similar, averaging 37 Ω, and the present one of one U-shaped tube of 50 Ω, while the lengths of the tubes did not differ much. The appearance of the potential difference was therefore, on our supposition, to be expected in the last case at a slightly smaller current than in the first; on the other hand, the greater length which was partly compensated by a greater section, made it probable that in the Oct. experiments the potential difference at the same temperature and current would be a few times larger, though not as much as seven times.

§ 4. *Questions to which the experiments give rise.* There were not sufficient data to make out whether the resistances used really differed as much as was thought as regards the opportunity of receiving heat through heat conduction from elsewhere, in particular Joule heat. It would however have to be regarded as a curious coincidence that this conduction of heat in conjunction with other causes had led to such a close correspondence in the phenomena observed. It seemed much more probable that the phenomena were to be accounted for not by disturbances from outside, but by resistance arising in the thread itself.

Where such a remarkable change in the condition of the mercury takes place as is shown by the disappearance of the ordinary resistance, the appearance of a "threshold value" dependent on the temperature naturally gave rise to the question, if we had to do with a deviation from Ohm's law [1]) for mercury below 4°.19 K. The electron theory, supplemented by the hypothesis in Comm. No. 119, that the resistance is caused by Planck's vibrators [2]), and by the more special hypothesis that the electrons move freely through the atoms as long as they do not collide with the vibrators and are reflected as perfectly elastic bodies at the surface of the conductor, indicates causes which might work in that direction. The distance which the free electrons travel between two collisions at which they give off energy derived from the electric force, might become comparable to the dimensions of the conductor below 4°.19 K. (compare Comm. No. 119 Feb. 1911 § 3, last note); the speed which they acquire in the electric current is perhaps no longer negligible compared to the velocity of the heat movement; for a certain current density at each temperature it might be just sufficient to bring the vibrators into motion, which otherwise below 4°.19 K. are stationary [1]). Considering all this, we may not take it as a matter of course, that OHM's law will still hold below 4°.19 K. and a further investigation of this will be interesting, if it only proves that this is actually the case.

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[1]) I hope to return to the new and important theory of Wien, in a further comm.

[2]) Lenard has recently given two important papers on the conduction of electricity by free electrons and carriers, which intend with a third paper to make a whole of his highly interesting researches on the interaction of electrons and atoms and the theory of metallic conduction. This gives to the latter a new and very promising base. In the first paper Ann d. Physik 40 p. 414, 1913 he comes to the result making use of the great conductivity of metals at helium temperatures (Comm. N⁰. 119) that Ohm's law is only valid within narrow limits for metals at very low temperatures comp. further VIII § 16 of this Serie. [Note added in the translation].

As long as the contrary is not experimentally proved, we shall however adhere to this law, because we have first to try to refer the phenomena as much as possible to already known ones and so far under appropiate suppositions from the domain of known phenomena the results obtained did not seem incompatible with OHM's law.

Various possibilities presented themselves at once. A very small residual resistance evenly distributed throughout the whole thread might remain, which might be peculiar to the pure metal as such (§ 12α), or might be the consequence of an admixture (mixed crystals) evenly distributed through the metal. It might also be that the pure metal in the particular condition in which it comes below 4°.19 K. and in which the atoms perhaps form one whole together, does not possess any resistance at all, but that somewhere (§ 11) in the thread through some peculiarity a section is sufficiently heated by great current density, to bring the temperature of the thread locally up to the vanishing point. In either way an ordinary resistance could be formed somewhere, which, when the strength of current is further increased, gives rise to an accelerated heat evolution and an increased development of resistance.

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[1]) At the great current densities that were attained in some of the experiments (see § 7), (they went up to 1000 Amp. per mM^2) the question arises if even the change in the resistance of the conductor through its own magnetic field of the current through the conductor should be considered, as it might be the case, that the resistance in the magnetic field for mercury in this condition was much greater, just as it alters with the temperature for some other substances, and has been found to increase for mercury at hydrogen temperatures (KAMERLINGH ONNES and BENGT BECKMAN, Leiden Comm. N⁰. 132*a*.)

§ 5. *Further investigation of the potential difference phenomena, in particular at temperatures slightly below the vanishing point.* It was considered desirable in the first place, to investigate the influence of the thickness of the thread upon the temperature, at which the fall of resistance occurs, and also upon the more or less sudden disappearance of the resistance.

The resistance apparatus with which the experiments (Jan. 1912) for this purpose were made differed from those of Dec. 1911 only in this, that in the two pairs of mercury threads which serve for the measurement of the resistance of the mercury (two current leads and two potential threads) the pieces that were above helium temperature were replaced by copper wire, in this way that the mercury legs were cut off and sealed up, and in the sealed up ends, as in the resistances of Oct. 1911, platinum wires were sealed in, which were in their turn joined to copper leads [1]). During the experiments all these contacts were immersed in liquid helium, compare fig. 3. This change was made since

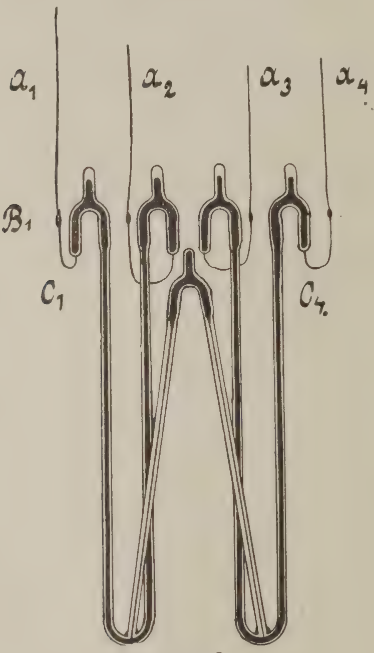

Fig. 3.

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[1]) The wires were made comparatively fine, to prevent the liquid helium from evaporating too quickly from the conduction of heat Besides the conduction of heat from above the absorption of radiated heat by the metal in the transparent apparatus was avoided. Later on, when the various circumstances could be better surveyed, leads were constructed which could carry a strong current without causing too much evaporation.

it had been shown that the kind of lead had little influence on the phenomena, so as to be free from the troublesome thermo-currents in the potential wires, when these were of mercury from the resistance which was immersed in helium to where the ordinary temperature began, and all four were replaced in order to be free in the choice of the pair of threads which were to be used as potential wires or as current leads. The thermo-powers were now only about 10 microvolts.

The experiments of Jan. 1912 were made with two mercury threads, one with a resistance of about 50 Ω, the other of about 130 Ω. These resistances were joined up in a circuit with a milliammeter, which could be shunted, and to each of them one of the coils of a differential galvanometer was connected as a shunt. By using only one coil at a time the resistance of each of the mercury threads could be measured separately; by connecting the two coils in the opposite direction the change in the ratio of both with the temperature could be investigated as long as the difference was small.

The ratio

$$\left(\frac{W_{130}}{W_{50}}\right)_{T=290^\circ} = \frac{128.4}{50.4} = 2.55$$

became, through cooling to the boiling point of helium

$$\left(\frac{W_{130}}{W_{50}}\right)_{T=4^\circ.25} = \frac{0.0542}{0.0249} = 2.18.$$

The ratio changed, as had been found before, and as could be readily explained by a slightly different manner of freezing of the mercury in the two tubes.

On changing the current strength at 4°.25 K. we found

Current in Amp.	W_{130}	W_{50}
0.006	0.0545	0.0251
0.010		0.0250^5
0.016		0.0249
0.030	0.0549	0.0260 ¹).

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¹) As regards the deviation at 0.03 amp. of W_{50}, we may perhaps conclude from the comparison of the ratio of the resistances at $T = 290°$ K. and $T = 4°.25$ K. in both resistances, that there is a thinner place in the thread W_{50} by which a greater heating takes place locally at temp. above the vanishing point, than would be expected from the average section.

Up to currents of 0.03 amp. therefore it is confirmed that there is no reason to assume a deviation from OHM's law above the vanishing point.

On lowering the temperature from the boiling point to where the disappearance of the resistance begins, this ratio remained unchanged according to the observations with the differential galvanometer; from that point downwards the resistance in which the current density was smaller, disappeared more quickly.

Although the resistance in the experiments disappeared gradually, yet the way in which it disappears gives the impression that the change in resistance of the mercury with the temperature occurs suddenly and that the gradual disappearance of the potential is due to the fact that the thread is only gradually cooled over its whole length to below the vanishing point, and only that part which is below this temperature looses its resistance.

It was again confirmed that at temperatures some tenths of a

TABLE II.

Resistance of mercury threads carrying current in the neighbourhood of 4°.2 K.

T	3.7 amp./mm^2 W_{130}	1.6 amp./mm^2. W_{50}
4°.24 K.	0.0532	0.0244^5
4.22	459	182
216	314	0.0069
214	264	34
213	190	13
210	128	0.0003
207	0.0087	1
205	50	1
201	46	0.0000
196	21	0.0000
190	0.0005	0.0000
180	0.0000	0.0000

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degree below the vanishing point no resistance was found up to very high current densities. Table III may be compared with Table I. In W_{130} the current centrur density could be raised to 400 amp. per sq. mm. without the least resistance being perceptable. The highest limit for the resistance is hereby put back at 3°.6 K. to $< 4.10^{-10}$ of the value at 0° C. (in the solid state) and reduced to about half of that to which we could go down in the January experiments.

TABLE III.

Potential differences at the extremities of mercury threads carrying a current. $l = 20$ cm.

$\pi r^2 = 0.0016$ mm² for W_{130}

$= 0.004$ „ „ W_{50}

Temp.	Current density in amp. per mm².		Potential difference in microvolts.	
	W_{130}	W_{50}	W_{130}	W_{50}
3°.6 K.	375	160	0	0
	490		0.27	
	500		2.12	
	625	260	12.9	0

For W_{50} at a strength of current of 1 amp. the current density which in W_{130} appeared to be the threshold value was not yet reached. A stronger current was applied. But now a special disturbance arose: on raising the current to 1.5 amp. so much Joule heat was generated by the current in the platinum wires joining the mercury leg, that this reached the thin mercury thread and brought it up to a temperature above the vanishing point. All this was accompanied by a rapid boiling of the helium, while the ammeter showed a strong falling off of the main current corresponding to a decided rise in the resistance. From the readings it could be seen that the resistance of W_{50} had risen to that which it has at hydrogen temperature This time it seemed most probable that the potential differences could be attributed entirely to heat introduced from outside, so that if this could be prevented it would be possible to bring at these lowest temperatures the highest limit for the possible residual resistance still nearer to zero.

§ 6. *Experiments with an apparatus arranged so as to be sure that no heat penetrates to the thread from places at a higher temperature than that of the vanishing point.*

A mercury resistance was made, suitable for observing the potential changes, when a current of 3 amp. went through the same mercury thread as in the last experiments, and to make certain that the disturbances which had occurred would be impossible. The mercury thread *C*, see fig. 4, at the ends of which the potential was to be measured was for this purpose lengthened at both ends by an auxiliary mercury thread of larger section. We will call these auxiliary threads *A* and *B*.

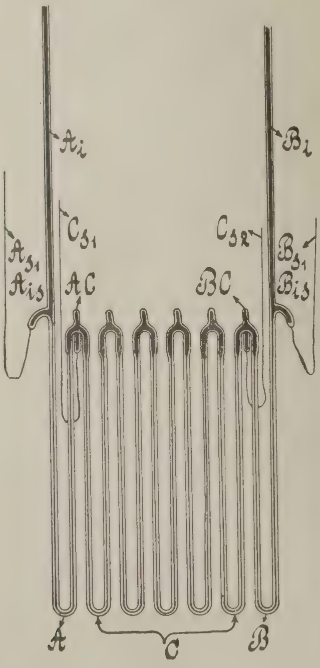

Fig. 4.

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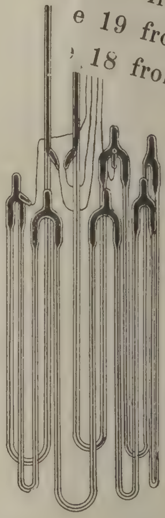

Fig. 5.

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By measuring the potential difference at the extremities of both auxiliary threads it could be ascertained that any heating above the vanishing point could not be the consequence of the introduction of heat which had entered the extremities of the resistance C which was to be examined through conduction. For this heat could only enter through the sentinel wires, and these could only become dangerous for the experiment after betraying a heating above the vanishing point by showing a potential fall.

On the ground of the experience in the last experiments, the connecting wires carrying the current in to the resistance (compare the diagrammatical fig. 4 and the perspective fig. 5) were again of mercury, in order to prevent JOULE heat being transported to the resistance while sealed in platinum wires to which copper wires were soldered served as potential wires. The sentinel thread A had at the ordinary temperature about 35 Ω, the sentinel thread B about 36 Ω resistance, the resistance C consisted of five threads in series of about 80 Ω resistance each and with a combined resistance of about 390 Ω at ordinary temperature.

At the boiling point of helium $W_{SA} = 0.01831\ \Omega$, $W_B = 1.01285\ \Omega$, $W_C = 0.1773\ \Omega$. The observations were as shown in Table IV.

We had therefore not succeeded, as had been our intention in giving a larger section to A and B than to C, in managing that if C should show potential difference, it would do so before A and B did it. Only if this had happened would it have shown that the heat that brought C to a temperature above the vanishing point was developed inside C. And the potential which now appeared in C can again be ascribed to heat conduction through A. The experiment shows very clearly that accidental circumstances in the freezing of the mercury threads play a part in the determination of the "threshold value" of the current density, and that in calculating with the average section of the tube in which the thread is frozen, only a lower limit can be given for this.

Possibly the mercury in A and B was only frozen in an unfavourable form, and therefore greater local current densities or worse exchange of heat had arisen than the average.

TABLE IV.

Resistance of a mercury thread just
below 4°.20 K.
$\pi r^2 = 0.0025$ mm² for W_C

Temp.	W_{SA}	W_{SB}	W_C
	current density 2.5 Amp. p. mm² in W_C		
4°.24			0.163 Ω
4 .234			0.161
4 .230		0.011	0.158
4 .222		0.0078	0.0774
4 .208	0.0022	0.0025	0.00775
4 .192	0.000024		0.000024
4 .185	0.000012		$< 10^{-6}$
	current density 12 Amp. p. mm² in W_C		
4 .185	0.000071	0.000153	$< 10^{-6}$
	current density 20 Amp. p. mm² in W_C		
4 .185	0.000117		0.000048

§ 7. *Repetition of the experiment with the same apparatus.* We obtained more favourable results from another freezing. First a few results may be given, which were obtained by measurements at different strengths of current at 4°.25 K., that is at a temperature above the vanishing point. These results gave an opportunity of judging to what degree heat can be given off by the mercury thread closed up in a glass capillary or flows off along the extremities.

From the increase of resistance at greater current strength, the rise of temperature was deduced on somewhat simplified suppositions, at which the equilibrium between the Joule heat and the heat given off to the outside is established. The result for the resistance and the average rise of temperature of C was:

current	resistance	rise of temp.
0.006 amp.	0.1928	0°.
0.006 „	0.1932	0°.
0.356 „	0.2149	0°.12
0.500 „	0.2410	0°.25

The average rise of temperature was calculated by the formula got by separate determinations

$$W_T = W_S\left(1 + 0.9\,(T - T_s)\right)\,^{1})$$

in which T_s represents the boiling point of helium.

It follows from these determinations that per degree of difference of temperature between mercury thread and bath 0.057 calorie is given off per second. If we assume that all the heat goes through the glass, that the mercury touches the glass everywhere, and that we only have to consider the narrow capillary, then we find with $d_i = 0.056$ mm, $d = 2.07$ mm, $l = 100$ cm, for the conductivity of glass $k = 0.00033$, while at ordinary temperature $k = 0.0022$.

The loss of heat through the glass must therefore by cooling to the boiling point of helium have become much less than at ordinary temperature, which might possibly be the consequence of the mercury only touching the glass at a few places besides in the bends.

The application of the data obtained at temperatures below the vanishing point is in the nature of the matter uncertain, as we do not know whether, with the galvanic change in the mercury, there may not be another change in the thread, which would bring about a further change in the giving off of heat.

With regard to the appearance of potential differences at the extremities of the thread, we found the data contained in Table V.

At 3°.6 K. the current at which a potential difference would appear in the sentinel wires could not be measured, as, before

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[1]) See the fig. in Comm. No. 124. Dec. 1911.

TABLE V.

Strength of current at which the potential difference appears at the extremities of a mercury wire carrying a current below 4°.2 K.
$\pi r^2 = 0.0025$ mm² for *C*.

Temp.	*A*	*B*	*C*
4°.18 K	0.0535	0.0615	0.034
4 .10	0.232	0.317	0.172
3 .60			1.068
3 .28			1.646
2 .45			2.56

the current had reached this value, the resistance *C* was heated to above the vanishing point along too great a length.

What we were aiming at was however attained in these experiments of Feb. 1912. It is established that heat is produced in *C* by raising the strength of current sufficiently, and that the heat is not conducted to it from *A* and *B*, since *A* and *B* were at a lower temp. than the vanishing point as appeared by the absence of potential fall in them. It is developed in the thread itself.

Table VI may be subjoined concerning the experiment at 2°.45 K corresponding to Tables I and III.

At the same moment that the galvanometer which measures the potential difference at the extremities of the thread is deflected, the strength of current in the main circuit falls from $i = 2.84$ amp. to $i = 1.04$ amp. which corresponds to an increase of resistance $\Delta W = 2.44\,\Omega$ in the circuit, from which it appears that the resistance is heated nearly to the temperature of hydrogen by the remaining current, of 1 amp. nearly

If we take the last described experiments together, we have been able by them on the one hand to raise the current density to the enormous value of about 1000 amp. per mm², without any heat being developed in the wire. This threshold value for

p. 23 line 16 from the bottom: for 2°.25 read 2°.45.
line 13 from the bottom: for *hat* read *had*.

TABLE VI.

Potential difference at the extremity of a mercury thread carrying a current below 4°.2 K.

$\pi r^2 = 0.0025$ mm^2

Temp.	current density in amp. per mm^2	Potential diff. in microvolts.
2°.45 K.	944	< 0.03
„	1024	0.56
„	1064	1.5
„	1096	6.3
„	1120	very large

the current density brings the highest limit for the possible resistance of mercury in the peculiar condition into which it passes below 4°.19 K. and particularly when it is cooled to 2°.45 K. still further back, and the ratio of the resistance at 2°.25 K. to that of solid mercury at 273° K. becomes $\frac{W_{2°.45\text{ K.}}}{W_{273°\text{ K.}}} < 2.10^{-10}$.

On the other hand it is proved that the *development of heat* which appears at a still higher strength of current, *hat its origin in the thread itself.*

§ 8. *Influence of the current density upon the manner in which the resistance in mercury threads disappears.* What has been related above can all very well be reconciled with the view (see § 5) that the disappearance of the ordinary mercury resistance at 4°.19 K. occurs quite suddenly, and in a thread that has been cooled to below that temperature, as soon as the "threshold value" of the current density is exceeded, somewhere heating occurs which carries the thread at that place to above that temperature, at first over a scarcely perceptible length but at higher currents over a rapidly increasing distance, by which ordinary resistance is generated in this part of the wire. With these larger currents the thread then comes in a state on which there is no uncertainty, it assumes over its entire length the new temperature equilibrium of a thread carrying a current, which equilibrium is determined above the vanishing point in the usual way. In order to improve the comprehensive view that may be formed on the ground of Table IV combined with Table II in which latter the different current densities do not refer to the same wire, further experiments were made in June 1912, which show how with the same thread the resistance disappears at different current densities.

The thread had a section of about 0.003 mm^2., at the boiling point of helium the resistance was 0.1287 Ω. The experiments were made with a falling temperature, with current densities of 1.3, 13 and 130 amp. per mm^2. (strength of current 4,40 and 400 milliamp). The phenomena are shown in the accompanying figs, upon which the numerical values are distinct enough to make it unnecessary to print a table. Fig. 6 allows a comparison between the phenomena at 0.004 amp. and 0.04 amp., fig. 7 at 0.004 amp. and 0.4 amp. The ordinates represent the potential fall in microvolts divided by the strength of the current, expressed in 0.004 amp., the abscissae the difference of the temp. T with that of the boiling point $T_s = 4°.25$ K. in thousandths of a degree. The unit of the scale of the abscissae in fig. 7 is five times as large as in fig. 6.

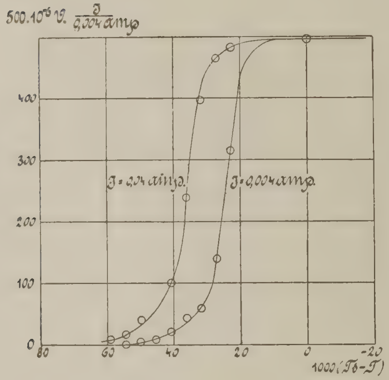

Fig. 6.

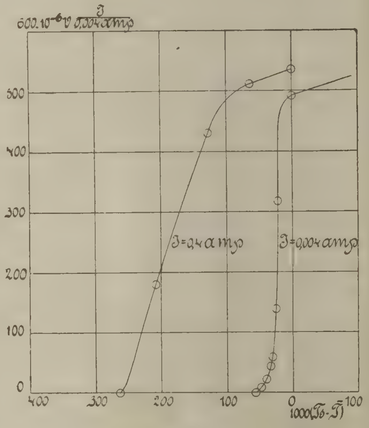

Fig. 7.

At 0.04 amp. the curve continues with diminishing values of the ordinate to lower temperatures than are shown on the fig.; at 4°.11 K., when the experiment had to be stopped, the resistance was not quite 0, we found $0.2.10^{-6}$ V. The intersection with the horizontal axis in fig. 7 is probably drawn too sharp; at 3°.96 K. the potential difference was $< 0.03.10^{-6}$ V.

The whole gives one the impression that the lower temperature of the bath at greater strength of current is required (a comparison of 0.004 and 0.04 amp. shows that an almost constant shift of temperature would change the potential differences per unit of current in the one case into those of the other) to cool the part of the thread that has an ordinary resistance strongly enough to prevent it imparting its temperature to the part which is below the vanishing point, and to prevent the temperature in the latter part from being raised above the vanishing point by the greater local development of heat.

With the same thread in the manner of table III the results of table VII were found, in which experiments are included with a second thread with a section of about 0.012 mm².

It appears that in the thread W_I, to which the experiments just quoted refer, local heating takes place more easily at the same current density than in W_{130} (see § 5). The fact that the latter thread gives off heat more readily also explains why in W_{130} a greater current density checks the disappearance of the resistance less than in the case of W_I (June 1912).

As regards the threshold value of the current density for different temperatures with the same thread, it would seem from Table VII and Table V roughly speaking to change linearly with the temperature, if the fall below the vanishing point is not too small, and if we leave out of account a term for JOULE heat which only appears distinctly at a higher current strength. This naturally suggests that we are dealing with a PELTIER-effect raising the temperature till the vanishing point of resistance (e. g. connected with different forms of crystallisation or tensions); (the simultaneous cooling of the opposite contact has no effect on the resistance which is already practically zero and remains zero when further cooled). As regards the threshold value of the density at a given temperature for different threads this appears (comp.

TABLE VII.

Potential differences at the extremities of mercury threads carrying current.

Temp.	Current density in amp. per mm^2		Potential difference in microvolts.	
	w_I	w_{II}	w_I	w_{II}
3.6 °K.		129		0.5
		141		very large
	363		0.3	
	412		3.8	
	429		12.1	
	431		very large	

§ 6 and Table IV) to be rendered uncertain by accidental circumstances. But it deserves notice that it was also found very high in very narrow capillaries.

(To be continued).

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 133^b.

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H. KAMERLINGH ONNES. Further experiments with liquid helium. H. On the electrical resistance of pure metals etc. VII. The potential difference necessary for the electric current through mercury below 4°.19 K. (continuation).

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **22 Maart 1913**, p. 1388—1391).

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H. KAMERLINGH ONNES. *Further experiments with liquid helium.* H. *On the electrical resistance of pure metals etc.* VII. *The potential difference necessary for the electric current through mercury below* 4°.19 K. (continuation).

§ 9. *Experiments on impurities as a possible source of disturbances.* Although the greatest care was always bestowed upon the purification of the mercury, the explanation of the appearance of a residual resistance that offered itself the first for closer investigation was the influence of impurities. These may give an "additive mixture resistance" to the metal which changes little with the temperature and is proportional to the amount of impurity. To such an additive resistance I ascribed the fact (Comm. No. 119 and Suppl. N⁰. 29) that the resistance of very pure platinum and very pure gold did not disappear at helium temperatures as I expected with absolutely pure metals. Now the experiments had realized the expectation, that mercury could be so far freed from impurities, as to make the resistance practically nothing. But if one may judge by the additive resistance which even very pure gold exhibits, then with the residual resistance of mercury which is only perceptable at the threshold value of current density for the lowest temperatures, it would be a question of an impurity of the order of a millionth of the trace that could possibly be present in the most carefully purified gold. And it was a priori doubtful if the mercury could be procured in so much greater a state of purity than gold. ¹)

The experiment was therefore repeated with solid mercury in which I believed a very small quantity of an other metal to be present. After being distilled in a vacuum by means of liquid air, the mercury was in one case brought into contact with gold and

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¹) On difficulties inherent in the supposition of a resistance equally distributed throughout the thread which apply also to our present case of additive mixture resistance see § 11.

the other time with cadmium, after which it was mixed with a larger quantity of pure mercury. To my surprise with the mercury that had been treated in this way, the resistance disappeared in the same way as with pure mercury [1]; much of the time spent on the preparation of pure mercury by distillation with liquid air. might therefore have been saved, without the experiments on the sudden disappearance of the resistance which were made with mercury prepared in the ordinary way with double distillation giving other results.

Even with the amalgam that is used for the backing of mirrors, the resistance was found 0 at helium temperatures. Later Dec. 1912 it was found that it disappeared suddenly, as with the pure mercury but at a higher temperature [2].

Where the influence of impurities, in the form of mixed crystals in the solid mercury, seems to retire into the back ground, the next most natural supposition is that less conductive particles, separated out of the mercury during the freezing, or coming amongst the mercury crystals in some other way, bring a resistance into the path of the current. But if we do not assume that a thread of perfectly pure mercury can possess a residual resistance itself, this theory of the origin of the potential differences is not very probable, because in a resistance-free path of current, only by a closing of the whole section by an ordinary conductor is resistance produced. Particles of the sort we mean, as also other casual circumstances, for instance the manner of freezing and small cracks, can influence the magnitude of the threshold value of the current density derived from the experiments, but the values found for this quantity, although they vary, differ so little, that in addition to the causes mentioned we must assume for a *thread* of pure mercury the existence of a residual resistance which we will call a "microresidual" resistance, to distinguish it from the "additive mixture" resistance to be attributed to impurities.

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[1] Perhaps not even a quantity of the order of a thousand millionth of zinc or gold is absorbed in solid mercury. The application of the sensitive test of the disappearance of the resistance may be of value for the theory of solid solutions. Of course in our argument we only deal with absorption in a form which comes into consideration for the resistance (mixed crystals).

[2] This part of the text is changed in the translation in accordance with the facts see § 13γ in VIII of this series.

p. 30 line 13 and 14 from the top: after "it was found" read: that if it disappears suddenly, as with the pure mercury, this happens at a higher temperature.

line 8 from the bottom: add: If this microresidual resistance is not evenly distributed over the thread (cf § 11), yet being a property of pure mercury itself, we will call it an "apparent microresidual resistance".

§ 10. *Experiments on the possible influence of contact with an rdinary conductor upon the superconductivity of mercury.* In the easoning that we have just given it is assumed that the laws of urrent division between two conductors which touch each other lso hold when one of the conductors consists of mercury below °.19 K. But this assumption might not be correct. In the line f thought of § 4 and taking into account the heat motion which akes the electrons now to the inside and then to the surface of he conductor, a pushing forward of the electrons in the galvanic urrent through a superconductor without performance of work eems only possible, when its surface only comes into contact with an insulator, which reflects the electrons with perfect lasticity. If the electrons can hit against the atoms (or more ccurately the vibrators) of an ordinary conductor, they will of ourse give off work in this collision. Thus a thread of superconucting mercury, if an ordinary conducting particle were present nywhere in the current path, could show resistance at that spot, ven although the particle did not entirely bar the section which was otherwise free from resistance.

These considerations lead to the following experiment. A steel apillary tube, supplied with connecting pieces in which were platinum wires for measuring the resistance, was carefully filled with mercury at the air pump. The measuring wires were immersed n the mercury, without touching the current wires. According o the ordinary laws of current distribution the resistance of this omposite conductor should disappear below 4°.19 K. Whether he mercury is in a glass or a metal capillary makes no difference o the conduction. Thus for instance, if one was to coil up such steel capillary filled with mercury, and press the coils against achother without insulating them, the coil could still serve as a magnetic coil below 4°.19 K.; the coiled up mercury thread would be resistance-free, and the steel would take the part of the insulator, which otherwise separates the different windings of the current ath in a magnetic coil. On the other hand if the above reasoning s correct, a mercury thread, that is provided with a close tting steel covering should retain its resistance below 4°.19 K. hough the current is lowered below the threshold value.

In several experiments with the above mentioned steel capillary, in accordance with the last conclusion, the resistance of the mercury thread did not disappear. Yet we must not conclude from this that the remaining resistance is given to the mercury by the contact with the steel. There only needs to be one little gapin the mercury which extends over the whole section, to cause the appearance of ordinary resistance of the amount according to the potential difference. If the resistance had disappeared in the experiments, there would on the other hand have been room for the question whether there had been contact between the steel and the mercury. With mercury in a steel capillary the result of the experiment remains always doubtful. We may therefore mention here, that afterwards when it was found that the resistance of tin dissappeared suddenly too, we succeeded in making a less doubtful experiment than is possible with mercury, with a flattened out constantin wire, which was covered with a thin layer of tin 1). The resistance of the layer of tin disappeared with a weak current and at a low temperature, while the constantin remains an ordinary conductor at that temperature.

Thus we may for the present adhere to the usual laws of current division, and in this extreme case continue to assume that in so far as the appearance of the potential difference is to be explained by a local heating in consequence of a local change in difference of the chemical nature of the conductor from pur mercury this disturbance must extend over the whole section the current path. Thus the conclusion drawn in § 9 concerning the probability of the existence of a microresistance remains valid.

(*To be continued*).

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1) It is to be noted, however, that the current density in the thin layer had to be made very weak. Comp the following part of this Communication VIII, § 16.

p. 32 line 5 from the top: for gapin read gap in.

p. 32 line 4 from the bottom, and p. 35 line 14 from the top: for microresistance read: microresidual resistance.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 133^c.

H. KAMERLINGH ONNES. Further experiments with liquid helium H. On the electrical resistance of pure metals etc. VII. The potential difference necessary for the electric current through mercury below 4°.19 K. *(Continued).*

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **31 Mei 1913**, p. 125—137).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES. *Further experiments with liquid helium.* H. *On the electrical resistance of pure metals etc.* VII. *The potential difference necessary for the electric current through mercury below* 4°.19 K. *(continued).*

§ 11. *Local nature of the loss of heat by a mercury thread enclosed in a glass capillary carrying a current, when the temperature sinks below* 4°.19 K. While the supposition that the thread should accidentally consist of some other substance than mercury for a small part of its length, is in contradiction to the regularity of the potential phenomena, yet on the other hand the supposition that the mercury thread has a microresidual resistance similar to the ordinary resistance in OHM's law (therefore independent of the strength of current, see § 4), gives rise to no less difficulties [1]. Such a microresistance proper to the mercury will be evenly distributed over the whole thread. If we calculate from the potential differences observed during the warming up at low temperatures and the strength of current to which they belong, the resistance of the thread under the conditions of the experiment, then we find that the thread, when the threshold value of the strength of current is only very slightly exceeded, must for a part of its length be partly heated distinctly above the vanishing point. Let us take for example the experiments of Dec 1911 in table I. We find from the threshold value of the current at 4°.19K., that the resistance of the thread at this temperature may be put at $< 3.10^{-6}\,\Omega$. In the experiment at 3°.65 K. we find that when the strength of current rises to 1 amp. the resistance, $11.5.10^{-6}\,\Omega$, was already distinctly greater than when the whole thread was at 4°.19 K., while the ends must still be at 3°.65 K. The portion that comes above the vanishing point by this heating, as it assumes ordinary resistance, need only be very small to produce the potential differences observed; in the case in point only 0.1 mm. If we assume that the giving off of heat to the bath may be calculated by the same data as were found for it above the vanishing point in § 7, then we find that, if the whole surface of the thread were at the mean of the temperature of the bath and of the vanishing point, the loss of heat per second should be about 20000 microjoules, while in reality only 14.0 microjoules, or about 1400 *times less*, are given off.

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[1] Besides those mentioned in § 9, the difficulties here treated also present themselves if we try to explain the potential phenomena by an even distribution of additive mixture-resistance.

We conclude from this that the rise of temperature in the thread, which is in a bath of a temperature below the vanishing point is only local. If there were anywhere else a rise of temperature (although of a smaller amount) the thread must have ceased to give off heat to the glass to a perceptible degree, except at certain points. The heat could therefore only flow to the extremities or the remaining points of conduction. This might be the consequence, for instance, of the mercury having come away from the glass everywhere except at the places indicated. But this is contradicted by the fact that in freezing the mercury adheres to the glass, and that immediately above the vanishing point the contact has not yet ceased. The supposition that everywhere where the temperature remains above the vanishing point (and perhaps close to it) the mercury thread gives off heat, and does not where the temperature is lower, is confirmed by the way in which the resistance disappears below the vanishing point (see Table II and fig. 7). If we determine, from the proportion of the resistance remaining to that just by the vanishing point, the length of the portion of the thread which is at the temperature of the vanishing point then the Joule-heat that it must give off at the existing strength of current corresponds more or less to that which is to be expected at the assumed difference of temperature of bath and vanishing point if the heat is given off to the glass over the whole length of that portion; more or less, for there remain unexplained and apparently systematic differences, with which perhaps the difference of the curves for different strengths of current in fig. 7 is connected.

In supposing, however, that the development of heat which brings a part of the thread to the temperature of the vanishing point is of a local nature, we give up the supposition that the microresidual resistance is evenly distributed over the thread. Assuming the whole of the path of the current to be of pure mercury, there could possibly only be an *apparent microresidual resistance*, in consequence for instance, of the mercury not being homogeneous, or not free from mechanical tension. These disturbances would then be the cause of threads showing a resistance throughout, while the pure homogeneous tension-free mercury would have an imperceptible microresidual resistance.

If we remember that with lead the increase of resistance by pressure [1]) becomes less at low temperatures, and has almost disappeared at hydrogen temperatures, then it is not probable that tensions, although they could cause PELTIER-effects, and although their regularity corresponds to that of the phenomena, should really play a part in the disturbances.

It would be more natural to suppose a lack of homogeneity in the thread, which might be the consequence of difference of the state of crystallization When we turn down a block of very pure KAHLBAUM-lead on the lathe, we can sometimes see a moiré effect on the surface, which indicates different alternating states of crystallization, each of which extends over more than a centimetre. In this way a thread of solid mercury might consist of a series of differently crystallized portions, the dividing surfaces of which would be at the same time usually cross sections of the thread.

At a dividing surface of this kind, a local heating such as we have treated above, might take place, at the expense of current energy. For instance a transitional resistance might give an apparent microresidual resistance to such a dividing surface. But the relation between the threshold value of current density and the temperature of the bath, points (see § 8) rather to a PELTIER-effect at this transitional place. We should then have to imagine that when the current density reaches the threshold value, the temperature at the dividing surface between two states of crystallisation, even if not high enough to occasion a thermoelectric force equal to the potential difference observed, yet reaches the vanishing point, and that, therefore, by further increase of the current density ordinary resistance must appear at this dividing surface. The length of the thread which takes an ordinary resistance would then increase with the excess of the development of heat above that which produces locally the vanishing point temperature; it would be further determined by the circumstances under which the excess of the heat developed would be given off. When we compare the potential difference observed in the different cases, there are one or two things that seem to confirm this supposition ¹).

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[1]) H. KAMERLINGH ONNES and BENGT BECKMAN. Comm. No. 132*b*. Nov. 1912.

Taking all this together, we are brought back to the idea that the potential phenomena must be ascribed to "*bad places*", although in a different sense to that in § 9. But the regularity of the phenomena remains a weighty objection to this hypothesis ²). For although, with the explanation of the local development of heat by a difference in the states of crystallization, the difficulty disappears which in the explanation by foreign resistances arose out of the circumstance that the whole section must be blocked up, still the appearance of a dividing surface between two states of crystallization is governed by chance. In any case, to come to an explanation on this principle, we should have to assume, that there are various PELTIER-places of the kind meant in each mercury thread of any length and that they are not too unevenly distributed.

But in this manner we would add a new indefinite hypothesis to the one which has to be tested and it is only by a complete quantitative working out of a perfectly definite theory that the question with which we are dealing can be answered: for the answer involves some far-reaching inferences. If we might assume that the potential phenomena in mercury-threads at a current density exceeding the threshold value are entirely due to disturbances then, on account of the systematic connection of the poten-

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¹) Too indefinite to be published.

²) The existence of a microresidual resistance is also made probable by that the ratios between the resistances for the mercury in the capillary tube and the frozen mercury thread at 4°.25 K. seems to run parallel to the threshold values, so that the difference of the threshold values might be ascribed to differences of the local deviations of the cross sections from the mean.

p. 38 line 6 from the bottom, and p. 44 note 1: for microresidual read real microresidual.

ial phenomena, there would be every reason to assume that we get a truer idea of the actual degree of conductivity of the superconductive mercury, the lower the temperature at which we determine the threshold value of current density of a thread [1]. And as at the lowest temperatures the disturbances still have an influence, although a smaller one, the actual conductivity would therefore have to be placed higher, perhaps a good deal higher, than the value found in § 7, which was already 0,5 . 10^{10} times that at the ordinary temperature, in other words the conductivity of the super-conducting mercury might *practically* be considered *infinite*.

§ 12. *Failure of the relations of* WIEDEMANN *and* FRANZ *and of* LORENZ *with super-conductors. α.* If the conclusion concerning the non giving off of heat to the glass by a mercury thread below 4°.19 K. which we discuted in § 11, were applicable we should arrive at a different view concerning the potential phenomena, from that arrived at above. If the mercury has an appreciable real micro-residual-resistance, so that heat is developed throughout the thread, and if we need not take any account of apparent micro-residual-resistances, the distribution of temperature in the part of the wire that is below the vanishing point, is governed by the ordinary formula for the rise of temperature of a wire conveying a current without external conduction of heat.

Let us keep as near as possible to the well known ordinary case in order to show the nature of the phenomena that are to be expected in the case in point, and for the sake of simplicity, as it is principally a question of order of magnitude, let us assume that below the vanishing point the ratio of the electric conductivity k to that of heat λ, is given by the same formula as holds approximately above the vanishing point, with the difference that the constant has a different value 10^7 times smaller, so that while above the vanishing point:

$$\frac{\lambda}{k} = aT \quad \text{with } a = 0.023.10^{-6} \text{ (watt. ohm. degree}^{-1}\text{)}.$$

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[1] In this train of thought there is no reason for not supposing that the conductivity assumes its large value immediately below the vanishing point.

below the vanishing point

$$\frac{\lambda}{k} = a'T \qquad \text{with } a' = a.10^{-7}.$$

We arrive at the low value which we ascribe to a' amongst other things in consequence of the fact that λ remains of the same order of magnitude below the vanishing point as above it, as appears when with the supposition that all the heat in the experiments is developed in the middle of the thread and only flows away at the extremities, we deduce an upper limit for the heat conductivity [1]).

With the assumption indicated the maximum temperature T_{max} of a thread, the extremities of which are at the temperature T_b, with a potential difference of E volts at the extremities is determined by

$$T^2_{max} - T^2_b = \frac{1}{4a'} E^2.$$

From this formula can be seen at once that the well known property of good conductors, that comparatively small potential differences, when external heat conduction is excluded, produce considerable heating, which may even lead to melting, becomes enormously more prominent in the superconducting condition.

In fact we find that at the smallest potential difference E of 0.5 microvolts, which is only a little above that which at 2°.45 K. is first observed, such comparatively great heating can take place, that even at the lowest values of T_b, T_{max} rises to 4°.20 K. At higher bath temperatures of course smaller potential differences are sufficient to reach the vanishing point, or at the same potential difference a' can be placed lower, at 4°.18 K. for instance $a' = a.\,10^{-5}$.

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[1]) This conclusion is confirmed by preliminary determinations of the heat-conductivity of mercury above and below the vanishing point made by Mr. G. Holst and me. We conclude from these that this constant does not undergo any considerable change at the vanishing point, and the same is true for the specific heat, which we have also investigated, however important the vanishing point may be for the electric conduction.

[Our preliminary yet very uncertain values are: for the conductivity between 4°.5—5° K., $k = 0.25$ cal. cm. sec., between 3°.8—4°.2 K., $k = 0.46$ cal. cm. sec., for the specific heat between 4°.2—6°.5 K., $C_p = 0{,}0014$ and between 3°— 4° K., $C_p = 0.00053$. (Added in the translation)].

p. 40 line 12 from the bottom: for lower read higher.

With the rough estimation of a' given, and assuming that the mercury thread where its temperature has fallen below the vanishing point gives off no heat to the glass [1]), we can, therefore, whithout the assumption of heating caused by local disturbances, predict phenomena such as threshold value of the current density and the differences of potential, that appear at greater current densities.

At current strengths below the threshold value, the thread will all along be in the condition of superconduction, without external heat conduction, at current densities above the threshold value this only exists for portions below the vanishing point temperature; for the portion of the thread that is above the vanishing point, the regime of ordinary conduction with loss of heat at the surface comes in its place [2]). In this way there can, however, be no question of the deduction of the law of dependence of the threshold value on the temperature, because it is determined by the temperature function, which we have arbitrarily assumed as constant a' while we have seen that in the train of reasoning followed it might have very different values at different temperatures, from $a' = 10^{-5}a$ to $a' = 10^{-7}a$. And it is very questionable if, when the necessary data are known for working out the sketch taking note 1 into consideration, the potential phenomena would correspond quantitatively to those observed. For the supposition with regard to the absence of external conduction of heat, upon which the theory in this § is based, might be untrue. (Cf. § 16 δ of VIII).

It would be of great importance [3]) to cool by immediate contact the thread over its whole surface with liquid helium; if the potential phenomena are to be ascribed to a real micro-residual resistance of the mercury, then the threshold value of the current density could probably be raised considerably higher than was now possible. This is too difficult with mercury. Thus for further experiments the use of tin and lead (see § 1) was indicated, these metals being more easily manipulated than solid mercury, and with them the conditions of the external conduction of heat being more easily regulated [1]. We shall treat of these investigation in future papers.

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[1]) This calls our attention to the question of the distribution of temperature along a thread through which a current passes without external conduction of heat for different laws of dependence of λ, k and T Laws might be imagined, which would cause the rise of temperature to run through the values from 0 to $T_{max} - T_b$ practically within a very small length of the thread, in which case the heating by a microresidual resistance could not be distinguished from a heating caused by a local disturbance. For the present, however, we adhere to the simpler supposition that the thread gives off no heat to the glass.

[2]) The divergence of the lines for 0.4 and 0.004 amp. in fig. 7 may also indicate the transition from the one regime to the other.

[3]) Less, when the particular circumstances mentioned in note 1 might exist.

β. We may here add a few remarks concerning the super-conducting condition.

The experiments described above leave no doubt that for mercury below 4°.19 K. there is no question of an approximate validity even as regards the order of magnitude of the relations established by WIEDEMANN and FRANZ and by LORENZ. The failure of this relation between λ, k and T indicates a difference between the super-conducting and the ordinary conducting state which may be regarded as a *characteristic difference* of both.

According both to § 11* and to § 12α, we come to a conductivity of mercury which is say 10^{10} times as great, or even more, than that at the ordinary temperature. If we assume that the number of free electrons per unit of volume at the transition from the ordinary to the super-conducting condition undergoes no important change, and then calculate according to the ordinary electron theory from the conductivity the free path of the electrons, we arrive at values which are comparable to the *lengths* of the mercury threads used in the experiments, in fact are considerably larger [2]. With such large free paths there would be every reason to believe that the peculiarities of the movements of the electrons pointed out in § 4, which are not consistent with OHM's law, would begin to play a part (which perhaps might resemble a PELTIER-effect such as seems to reveal itself in the potential phenomena). It is, however, questionable whether the whole hypothesis developed in § 4 in connection with Comm No. 119, concerning the movement of free electrons through the metal and which is also mentioned in § 10, must not be replaced by an essentially different one for the super-conducting condition, according to which the movement of the electrons is carried on by the current for considerable distances, but each separate electron which takes part in the progress, only moves one molecular distance.

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[1] The purity of both can probably not be made so high as that of mercury so that disturbances from a trace of additive admixture resistance in the super-conductive state do not seem impossible.

[2] Taking the free path at ordinary temperatures at 10^{-7} cm., it becomes 10^2 cm. at 2°.45 K., yet taking no account of the decrease of the number of free electrons. We do not consider collisions of the electrons mutually, as these would cause microresidual-resistance phenomena.

To illustrate this idea we may take as an example the well known case of the propagation of a blow by a row of billiard balls which just touch eachother. In a super-conductor the flow of electricity might consist in this, that an electron jumping across on to an atom of the super-conductor from one side causes an electron on the other side of the atom [1]) to jump into the next atom, etc. till finally at the further end of the superconducting wire as many electrons would be carried away in the direction of the current, as were thrown in at the beginning [2]).

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[1]) To express it more accurately, in the same layer of atoms taken across the path of the current, more passes over in a given time than is sent out (or thrown back) through the same layer in the same time to the side from which the electrons taken up come. We here give only the simplest possible sketch, to characterise the super-conducting condition.

[2]) The taking up of an electron on one side of an atom and the giving off on the other side of one to another atom, would then be accompanied by a moving up of the electrons (through or) over the surface of the atom, by which each electron moves along a part (if the number of electrons on the surface of an atom is large, then a small part) of the diameter of the atom· The connection of the electrons of two different atoms with each other and with these atoms probably does not differ very much from the connection between the electrons of one atom with each other and with the atom, so that the passing of an electron from the one atom to the other in the super-conducting state would be similar to the movement of the electrons in a single atom. The conductivity of the super-conductor would thus be that of the atoms united into one continuous whole (see § 4).

If the numerous electrons in the atom, which belong to the framework of it, in the described process only pass on the blow from the one electron that jumps onto the atom, onto the one that is given off without themselves taking part in the movement and if the moving electrons are the valency electrons, then our hypothesis, although arrived at by a different road, may be regarded as an application to the super-conducting state of the hypothesis of Stark concerning the movement of the framework of the valency electrons along the

The migration speed is thereby propagated through the superconductor without the performance of work [1]). If the super-conducting metal is converted into an ordinary conducting metal by heating above the vanishing point, (if the point is not much exceeded it will still be strongly conducting) then, according to this hypothesis the Ohm resistance is due to the action of the vibrators (between the atoms) which bring the atoms to a distance from eachother such that the electrons cannot jump from one atom to another without doing work, but in traversing the space made by the vibrators between the atoms give off some of the electric energy taken up by them [2]). The representation given of the conduction in the super-conductors seems thus to be most easily combined with the conduction theory developed by Lenard.

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shearing surfaces of the metal crystals. It thus shows the usefulness of the fundamental idea of Stark. As in the above hypothesis this idea is supplemented by the notion of the free moving electrons of the original electron theory viz. the jumping across of the electrons, the connection with the electron theories of the ordinary conducting state, especially with that of Lenard, is maintained.

[1]) In so far as we may disregard microresidual resistance.

[2]) We will not discuss whether this happens through electrons with migration speed being taken up and electrons without migration speed being given off or by elastic collision of the electrons against the surface of the atoms between which they move backwards and forwards: through energy of ordered motion being transformed into energy of unordered motion. We must remark that for the explanation of the super-conducting state the assumption that in contrast to non elastic collision in ordinary, only elastic collision takes place in the super-conducting state is inadequate. As Lorentz has taught us (comp. Reinganum, Heidelb. Akad. 1911, 10 p. 7) even with elastic collision the above mentioned transformation must take place and show itself as development of heat.

By the transition from the superconducting state to the ordinary in proportion as the atoms begin to vibrate separately in larger numbers and room is made for the movement of the electrons between the atoms, the mechanism develops which leads to the approximate relations of Wiedemann and Franz and of Lorenz. The communication of the movement of the electrons inside the atoms to eachother perhaps plays a chief part in the conduction of heat. The continuity of the heat conduction above and below the vanishing point would then be explained by the small change which the process undergoes when the peculiar connection of the atoms which makes super-conduction possible, is destroyed.

The change of the distance between the atoms also clearly plays a part in the change of the resistance at the melting point.

p. 45 line 4 from the top: for restistance read resistance.

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In my rough sketch (Comm. N°. 119) of the application of the quanta-theory to the electron-theory of conductors, in order to udge whether the hypothesis that restistance is caused by vibrators (the electrons otherwise moving freely through the metal with speeds in accordance with the kinetic theory of gases 1)) is well adapted to deduce the change of resistance with temperature, I put the mean free path of the free electrons inversely proportional to the mean amplitude of Planck's vibrators, which disturb them in their movements, while this mean amplitude was calculated by the formula which Planck at the time gave for the mean energy of the vibrators. The way in which mean values were introduced by this (comp. the reasonings in Wien's theory, which clearly show the deficiencies of mine) could not allow us to expect more than a qualitative representation. Yet, as is rather remarkable, a close agreement was obtained with the observations between the ordinary temperature and that of liquid hydrogen. It is more difficult to judge of the suitability of the new hypothesis for reproducing the observations with metals above the vanishing point. According to the note at the end of Comm. N°. 119 the energy of the vibrators would also determine the increase of the volume of the metal from $T = 0$. The mean distance of the surface of the atoms may thus perhaps be taken proportional to the square of the mean amplitude calculated according to Planck's just mentioned formula. We may perhaps further conclude that the idea of the condition above the vanishing point at which we arrived starting from the new hypothesis concerning the super-conducting state, will appear to be not unsuitable, and in any case gives no ground for objecting to the last named hypothesis.

On both assumptions, however, the assumption that the free path is continuously described by the same electron, and also the other that it is broken by the movement being transferred

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1) Keesom (this same Report, Suppl. No. 30*b*) has come to the important conclusion, by the application of the quanta-theory to the free electrons in a metal (considered as a monatomic gas) that at low temperatures the velocity of the free electrons becomes independent of the temperature, and has called this field of temperature the "Wien field."

over a distance from one electron to another, a difficulty arises in the explanation of ordinary resistance, because PLANCK's previous formula has been replaced by a new one. In the discussions at the Conseil SOLVAY [1]) (Oct. 1911) I pointed out that according to the theory developed in Comm. N°. 119, if we introduce the new formula, and further calculate in the same way, i. e. with only one frequency, the resistance could not fall below a certain value determined by the "internal temperature" (according to $\frac{h\nu}{2} = \frac{1}{2} k\beta\nu$ and $\beta\nu = 200^\circ$ K. for silver 100° K.) multiplied by $\sqrt{T}$, while above $T = 0$ (for various metals above helium temperatures) it seems to become practically nothing. We must therefore adhere to the old formula [2]) for calculating the amplitude, or rather, accepting the new formula on account of the more satisfactory representation that it gives in many respects, we must assume that the amplitude of the vibrators that comes into consideration for the determination either of the free path of the electrons through the metal or of the distance between the atomic surfaces (the part of the path between their old and their new positions, upon which the electrons experience resistance in their movement from one atom to another) [3]) is only determined by that part of the energy of the vibrators, which is dependent on the temperature. In addition, in order to explain the existence of the super-conducting state one would have to assume that when the excess of the energy above the zero point energy has fallen to the small value which corresponds to the temperature of the vanishing point, the resistance to the motion of the electrons between the atoms suddenly becomes zero [4]).

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[1]) La théorie du rayonnement et des quanta. Rapports et discussions de la réunion à Bruxelles sous les auspices de M. SOLVAY. Paris 1912 p. 129.

[2]) As WIEN does in his theory. Sitz Ber. Ak. d. Wiss. Berlin 1913. p. 200.

[3]) We may remark that it is not necessary that when an electron jumps over with resistance the whole surplus velocity which it has to propagate should be lost.

[4]) Perhaps the distance of the surfaces of neighbouring atoms has then become equal to that of two neighbouring electrons in the same atom (comp. note 2 p. 43) and the connection of the electrons of two atoms similar to that of the electrons in one and the same atom (comp. the speculations on "atom-fast" compounds in KAMERLINGH ONNES and KEESOM, Encyclop. d. Math. Wissensch. V 10, Leiden Comm. Suppl. No. 23 Nr. 57).

In the reasonings of Comm. N⁰. 119 it was assumed that all vibrators in the metal have the same frequency. As the resistance is mainly determined by $e^{-\frac{\beta\nu}{T}}$ one need only assume as the single difference between the super-conducting condition and the normal that the frequency of the vibrators is say four times higher in order to find at the vanishing point a micro-residual resistance 10^4 smaller than the ordinary resistance at the same temperature and at 2° K. one which is 10^9 times smaller. But against this explanation it may be adduced that in order to bring the formulae of Comm N⁰. 119 into agreement with the observations at the lowest temperatures the frequency has to be taken lower as the temperature falls [1]). WIEN in taking into account in the calculation of the free path of the electrons all the frequencies which play a part in the specific heat has succeeded in explaining this peculiarity: the resistance according to his theory diminishes at very low temperatures only as T^2 or as $T^{5/2}$, (depending on the choice of a subsidiary hypothesis). But then it becomes much more difficult to explain the extremely small value of the possible micro-residual resistance by considering the super-conducting metal simply as a metal with slightly modified properties. It thus seems as if at the vanishing point something occurs by which the small frequencies lose their influence on the resistance although they continue to play a part for the specific heat. The spectrum of the frequencies of the vibrators which are operative in the resistance would thus become limited to a few higher frequencies or at least be cut off on the side of the small frequencies, in the same way as this happens according to DEBIJE on the side of the high frequencies [1]).

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[1]) As I pointed out at the discussion of the Conseil SOLVAY (l. c. p. 298) one might suppose considering that the vibrations take place in the system of mutually connected molecules that there are two kinds of vibrations, a longitudinal and a transversal kind. Perhaps above the vanishing point only two vibrations play a part in the resistance, a transversal and a longitudinal one, so that according to PLANCK the small frequency becomes prominent at the lower temperatures, and at the vanishing point this frequency changes into a very high one, so that the original higher one assumes the more important part.

A rotation in opposite senses of two neighbouring atoms with small frequency above the vanishing point, might perhaps, by the atomic surfaces overlapping below the vanishing point, change into a rotation with high frequency. [The caloric investigation of what happens in passing the vanishing point will throw light on this question. As to the specific heat above and below the vanishing point compare the addition to note 1 page 40].

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[1]) This raises the question whether above the vanishing point also the small frequencies do not in some way lose their influence on the resistance all the more the smaller they are.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

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Director of the Laboratory.

N°. 133^{d}.

H. KAMERLINGH ONNES. Further experiments with liquid helium. H. On the electrical resistance etc. (*continued*) VIII. The sudden disappearance of the ordinary resistance of tin, and the super-conductive state of lead.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **31 Mei 1913**, p. 137—153).

Eduard IJdo — Printer — Leiden.

51 line 13 from the top: for 10 read 11.

H. KAMERLINGH ONNES. *Further Experiments with liquid helium. H. On the electrical resistance etc. (continued).* VIII. *The sudden disappearance of the ordinary resistance of tin, and the super-conductive state of lead.*

§ 13 [1]). *First observation of the phenomena.* α. Passing from the investigation of the super-conductive state of mercury to that of the change in the resistance of various other metals when they are cooled to helium temperatures, although I hoped to find more super-conductors, I did not think it likely, judging by our experiences with gold and platinum (see Comm. N^0. 119, III and Comm. N^0. 120, IV of this series) that we should be able to get more than a systematic survey of different cases of additive admixture-resistance (see Comm. VII of this series § 10). Very soon, however, the surprising results with tin and lead were obtained, which we mentioned in Comm. VII § 1 and § 12.

In the first place on Dec. 3rd 1912 we investigated a wire of pure tin, and perceived that this metal too, at helium temperatures became super-conducting.

The tin was of the specially pure kind supplied by KAHLBAUM. It was melted in a vacuum and poured into a glass capillary U-tube. The capillary tube had tin branches at either end, by which the conducting wires and the measuring wires were attached. The resistance at the ordinary temperature, 290° K., was 0.27 Ω.

We found that at the boiling point of helium a small ordinary resistance $1{,}3.\ 10^{-4}\ \Omega$ remained. At 3° K. this had disappeared ($< 10^{-6}\ \Omega$) and when the field of temperature between 4°.25 and 3° K. was gradually gone through, we found that the disappearance took place suddenly at 3°.78 K.

In order to be better able to judge of the micro-residual resistance, we tried to make a tin wire of greater resistance, in the same way in which we had formerly succeeded in making a long thin lead wire [1]). A steel core was covered with a substantial layer of pure tin, and turned down on the lathe. Then with a razorshaped chisel a thin spiral shaving was cut off [2]). This method, which seemed preferable to drawing (comp. § 14*a*) by which the metal might undergo a greater change, yields without difficulty wires of 0,01 mm^2. section. Several of these wires were then joined into one long wire by melting them on to eachother, during which it was necessary to carefully avoid the possibility of oxide being introduced into the surfaces to be united. The tin wires, one of which 1.75 m. long had a resistance of 19.2 Ω, and the other 1.5 M. long a resistance of 6,7 Ω, were wound upon glass cylinders, between a spiral of silk thread which separated the windings of the tin thread from eachother. Leading wires of tin fastened to the up turned ends of the wire, were lead downwards through the liquid and attached to copper wires. With these resistances immersed in liquid helium the sudden disappearance was observed when the temperature fell to 3°.806 K. (boiling under 47 cm. mercury pressure). At 3°.82 K. the resistance of one was still 0.0183 Ω, of the other 0.00584, at 3°.785 K. of both $< 10^{-6}\,\Omega$. In this case too the highest limit for a possible micro-residual resistance was thus very low. We may put $\frac{w_{3^\circ.8\,K.}}{w_{273^\circ\,K.}} < 10^{-7}$.

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[1]) The §§, tables and figures are numbered successively to those of Comm. VII of this series.

Besides the sudden disappearance of the resistance of the wire, we also observed, as in the mercury thread, that for each temperature below the vanishing point a threshold value for the current density [3]) determined by this temperature, (in the case of the last mentioned wire the threshold current was 0.28 amp. at 3°.785 K.) could be fixed, below which the current passes without any perceptible fall of potential, and above which it is accompanied by potential phenomena, which (see § 14) increase rapidly with the increase of the excess of the current above the threshold value In a word, the tin wire behaves below the vanishing temperature of the tin, 3°.8 K., qualitatively precisely the same as a thread of mercury below the vanishing point of that metal.

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[1]) KAMERLINGH ONNES and BENGT BECKMAN. Comm. No. 132*c*. Dec. 1912.

[2]) A few of the tin wires first made did not become super-conducting; the inferior method of working the metal had perhaps caused additive admixture resistance, or more probably very insufficient continuity of material.

[3]) Concerning the dependence of the threshold value upon the dimensions of the wire and the conditions under which the heat is given off, further investigation is needed.

β. Lead of KAHLBAUM, made into a wire in the same way as the tin, 1.5 m. long and 10.8 Ω resistance at ordinary temperature, when it was immersed in liquid helium appeared to be super-conducting, without the necessity of reducing the pressure at which the helium boiled. When the temperature was raised as far as the cryostat permitted, that is to 4°. 29 K. (the pressure was raised 11 cm. mercury above 76 cm.) the lead remained super-conducting. The temperature at which the ordinary resistance of the lead disappears will probably, as indicated in § 15, not be far above the boiling point of helium.

Whether this disappearance, as with mercury and tin, also takes place suddenly, has yet to be investigated. For temperatures below 14° K., where lead has still a relatively high ordinary resistance, and above 4°.3 K. where it has disappeared, we do not yet possess a satisfactory cryostat. At the temperature just mentioned of 4°.29 K. we found that the threshold value of the current was not yet reached at 1.3 amp.

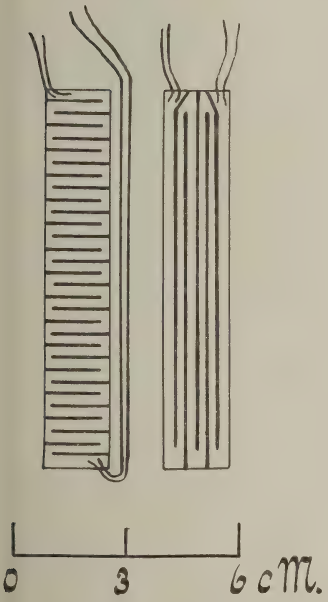

Fig. 8. Fig. 9.

γ. Besides lead and tin, amalgamated tin foil was investigated. We examined a layer of it spread out on a mirror glass, in which layer grooves were made in the manner shown in fig. 8. In helium boiling at atmospheric pressure, it appeared to have lost the ordinary resistance (2.3 Ω at 290° K.). At 4°.29 K. we found

0.12 amp. for the threshold value of the current, and a potential of 1.3. 10^{-6} volt, at 0.30 amp. 19.8. 10^{-6} volt, and at 0.363 amp. 34.6. 10^{-6} volt.

It is worth noticing that this tinfoil becomes more easily super conducting than either tin or mercury. Perhaps the soft tin-amalgam, though a solid solution (of mercury in tin), has this property. This would only need to become a continuous whole in order to provide a nonresisting path for the current beside that of the free mercury (comp. § 9) or tin that might be present in the tin foil.

§ 14. *Further investigation of tin.* The further investigati of tin and lead does not form by any means a complete whole yet. Several of the measurements we had in view were failures, so that the results attained are very disconnected; nevertheless, in connection with our experiments with mercury, I think them worth communicating.

α. Methods of working the tin. In the previous § we said that working the tin into a spiral shaving did not interfere with the sudden disappearance of the resistance. What is of even more importance is that the rolling out of the wire to a thickness of 0.01 mm. has not any influence upon the super-conducting state either, so that we may feel confident that a very thin nonresisting tinfoil could be made [1].

We must remark that in working tin, heating must be avoided. The increase of hardness which is caused in the drawing of metals by the compression and stretching, which is accompanied by an increase of resistance and decrease of the temperature coëfficient, is removed in gold and platinum for instance, by heating. With tin, on the other hand, heating is injurious, it causes the resistance to increase [2], moreover, it causes thin wires to go into angular

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[1] The resistance of commercial tin foil, pasted on glass and cut out as in fig. 9, appeared not to become zero.

[2] According to TAMMANN and his school, the crystals are shattered by wire drawing, and arranged in such a way that in the cases meant the resistance increases. By heating, larger crystals are again formed, and the resistance resumes its original value. In the investigations of KAMERLINGH ONNES and CLAY (Comm. No. 99*b*, § 4, June 1907), it is pointed out that the additive resistance o

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p. 54 line 5 and 10 from the top: for tin foil read amalgamated tin foil.

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orms [1]). The threads we used were, therefore, not heated after eing worked, and showed regular curvatures when bent.

β. Potential phenomena in the super-conducting state. The fol- owing observations allow us to judge of the highest limit of the ossible micro-residual resistance, and of the potential differences bove the threshold value of the current density just below the anishing point. They were made with a branching tin wire xactly like the one used in the experiments with mercury f Table IV and V in Comm. VI of this series, § 6 and 7. he resistance consisted of a principal wire W_C 4 M. long, and mainly .0097 mm^2. section [2]) with two sentinel wires W_{SA} and W_{SB} [3])

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latinum and gold wires is always found greater by continued drawing even fter heating to glowing. We attributed this to the acquiring of admixtures hrough the drawing. In gold it is possible to test for such small quantities f admixture as are here of importance. In gold wires carefully drawn by ERAEUS, (Comm. no. 99*c* § 2, June 1907), under repeated treatment with acids, arger quantities of admixtures were found in proportion as the resistance fell ess at reduction to hydrogen temperatures At the same time it is possible hat the drawing itself has an influence. HENNING (Ann. d. Phys. 1913), thin- king as we do, attributes the difference found with his platinum thermometers in the temperature coefficient from that found by us, to a larger amount of admixtures in our thermometer. The difference becomes greater still, when we consider that HENNING's wire (0.05 m.m.) was drawn out further than ours (0.1 m.m.) (which is of importance in the application to thermometry). As mentioned above and as we found confirmed in comparing the wires Pt_I (0.1 mm.) and Pt_d (0.05 mm.), thinner wires fall less in resistance, a result by which we also explained, l. c. why HOLBORN's thick wires (0.2 mm.) showed a greater fall than ours. Our wires were at the time most carefully drawn by HERAEUS from the purest platinum supplied by him. The platinum obtained by HERAEUS later on may have been even purer. Improvement may also have been made in the method of drawing the wires.

[1]) Where broken, tin wires exhibit comparatively large crystals. See also § 15, note 1.

[2]) In this investigation the section is deduced from the length of the wire and the resistance at ordinary temperature. We only ascertained, whether this agreed approximately with the result of direct measurement. The values given are therefore only to be considered as rough mean values.

[3]) The object of the sentinel wires was the same as in VII § 6. We had namely calculated on sending much stronger currents through than we actually did, and on that supposition it was necessary to make sure that no JOULE heat penetrated to the wire from elsewhere.

of 0.8 M. length and about 0.02 mm^2. section, wound round a glass tube and insulated with silk. We found, (Febr. 1913)[1]:

TABLE VIII.

Resistance of a bare tin wire at, and a little below 3°.8 K. Section of w_C: 0.0097 mm^2.

T	w_{SA}	w_{SB}	w_C
	Current density 0.61 amp./mm^2. in C		
3°.85 K.	$6.84 \cdot 10^{-3}\,\Omega$	$6.50 \cdot 10^{-3}\,\Omega$	$69.6 \cdot 10^{-3}\,\Omega$
.82	5.50	0.90	34.9
.79	2.82	0.03	1.23
.785	1.5	0	0
.78	0.7	0	0
.75	0.15	0	0
.74	0.02	0	0
.72	0	0	0
	Current density in C 154 amp./mm^2. (and higher ?)		
1°.6	0	0	0

With a coil of 252 windings of tin wire insulated by picëin (see § 16) of 0.014 mm^2. section, (with pieces of 0.02, 0.012 and 0.03) and 79 Ω resistance at ordinary temperature 290° K., the disappearance of the resistance was followed, at three different current strengths as in § 8 was done with mercury. We found:

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[1] In one of the sentinel wires W_{SA} there is obviously a thinner place which causes locally a much greater current density than the mean. Probably the same case occurs here as in the experiments with mercury in Table IV, but here the disappearance of the resistance at lower temperature makes it improbably that the tin wire should be interrupted by a foreign resistance.

TABLE IX.

Disappearance of the resistance of a tin wire, under reduced giving off of heat, at different currents.

T	0.004 amp.	0.04 amp.	0.4 amp.	0.6 amp.	1.0 amp.
3°.82 K.	0.0533 Ω	0.0535 Ω	0.0536 Ω		
.805	500	534	536		
.79	488	533			
.785	425				
.78	162	508			
.765	0.00137				
.75	0.00005	0.0039			
.74	1	14	0.0532		
.72	0.000000	0.00025			
.70					
.68		0.000012			
.66		0.000000	0.0050		
.64					
.54			38		
.42			22		
.28			10		
.12^5			0.0002		
2.69			0.000012		
.35			0.000000		
1.6				0.000000	great

This table gives in general the same as fig. 6 and 7 of § 8. The disappearance of the resistance extends over a much larger field of temperature than with the mercury thread, probably because the giving off of heat is considerably reduced by the winding up of the wire protected by picëin; which is probably also the reason why at the lowest temperature the strength of the current cannot be raised above 0.8 amp. and the threshold value of the current density therefore only reaches 56 amp/mm^2.

γ. Experiments concerning the influence of the contact with an ordinary conductor of a metal which can become super-conducting, upon its super-conducting properties, were in continuation of those of § 10 made with tin in two different ways, first with a german silver tube, which was tinned, and through the layer of tin of which a spiral was cut, and second with a constantin wire which was tinned. In the first experiment the resistance did not disappear, in the second, as already said in § 10, it did; from which we conclude that the continuity of the layer of tin in the first case was not sufficient. In the second experiment the threshold value was, however, also very low, even at the lowest temperature 1.°6 K. it remained below 0.095 amp. for the bare wire immersed in liquid helium. It is simplest to assume in the mean time, that the layer of tin becomes super-conducting, but that the section of it, which was: deduced from the resistance 0,0125 mm^2., according to measurements down to 0,1 mm^2., here and there was very small. There was in this case no reason to suppose a want of contact between tin and constantin, as in the corresponding experiment with mercury between it and the steel.

§ 15. *Further examination of lead.* In the first place we will mention a few experiments on the heating of a wire which was at a temperature below the vanishing point, which correspond to those in Table VI for mercury. The lead resistances were arranged exactly like the tin resistances described in § 14, the bare wires were wound upon glass between silk. With a wire of 0.025 mm^2. section (10.8 Ω resistance at ordinary temperature) containing six joints, which were made with a miniature hydrogen flame, we ascertained that joints do not interfere with the experiments. The results (Febr. 1913) with one of the wires (92 Ω at ordinary temperature) are contained in Table X (the observations were confirmed later on repetition).

TABLE X.

Potential differences in a lead wire carrying a current $l = 6$ m., section $= 0.014$ mm².

T	Current density in amp./mm².	Potential difference in microvolts.
1°.7 K	560	0.0
	645	0.2
	675	3.5
	695	5
	710	6
	720	10
	750	19
	791	± 40
	$>$ 790	very great

A similar experiment with the wire containing six joints at less low temperature gave:

TABLE XI.

Threshold value of current density for bare lead wire of section 0.025 mm².

T	Threshold value in amp. mm².
4°.25 K.	$>$ 420
	$<$ 940

At a current density of 940 the wire was dammaged (calefaction ?) and upon repetition it appeared that is was broken.

Similar conditions of external conduction of heat to those of the tin coil described in § 14, prevailed in a lead wire (see § 16) of 1000 windings (resistance at ordinary temperature, 290° K., 773 Ω) insulated by silk soaked in liquid helium. We found:

TABLE XII.

Potential difference in a lead wire carrying a current with reduced external conduction of heat.

$l = 55.5$ m. section $= 0.014$ mm^2.

T	Current density in amp./mm^2.	Potential difference in microvolts.
4°.25 K.	33	0.03
	36	0.65
	38	1.75
	40.2	7.35
	41.3	22.0
1°.7	60	3.7

Judging by this we may perhaps estimate that the lower limit of the threshold value at 4°.25 K given above cannot be raised much, and that the vanishing point for lead lies at about 6° K.

Further, measurements were made with lead wires placed in a vacuum, the object of which is obvious by § 12. The apparatus which served for this consist (see fig. 10 and fig. 11, face view and diagram of *d* with detail figures) of a glass reservoir immersed in liquid helium, carried by a long narrow glass tube fixed into the lid of the cryostat. The reservoir *d* can be evacuated through the tube *c* (the tap *a* allows it then to be connected to a tube filled with charcoal which is immersed in liquid air); through the indicator gauge *b* we can make sure that the apparatus is not cracked in cooling.

In the apparatus shown in the fig. there are two lead wires (see diagram); we were only able to do the measurements with one. Four short tubes are blown into the upper part of the reservoir to receive the lead wires (see detail figures); upon these tubes after platinizing and copperplating caps are soldered with tin into

Erratum Communication N⁰. 133.

p. 61 top line: for „hilium" read „helium".

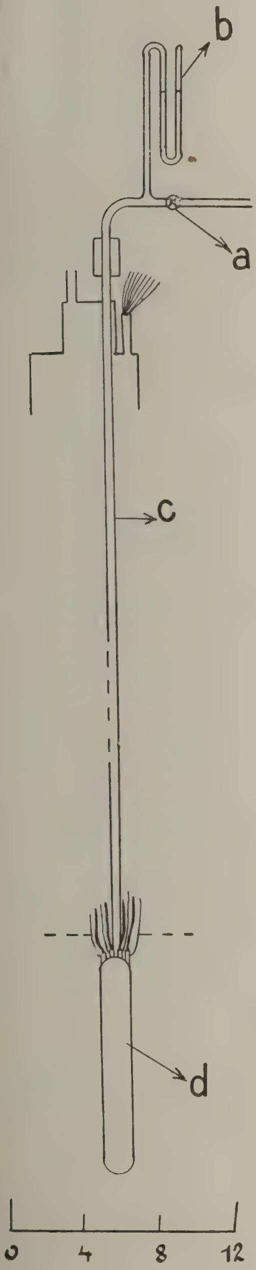

Fig. 10.

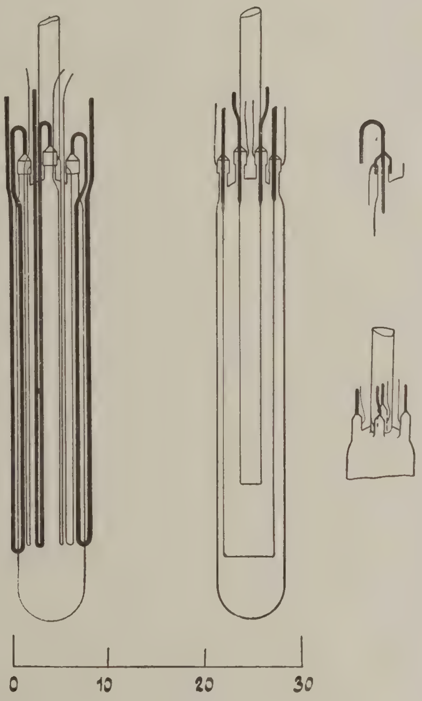

Fig. 11.

which the thicker top ends of the wires are soldered with WOOD-metal [1]).

Rolled out lead wires are fastened to the wires that project from the covers, and run down along the reservoir, insulated from each other with silk and then up again through the liquid helium.

We found with a part of the wire of Table XI:

TABLE XIII.

Threshold value of current density of a lead wire in vacuo; section $^1/_{70}$ mm^2.

T	Current density in amp./mm^2.
4°.25 K.	$>$ 270

The experiment is incomplete as the threshold value was not reached.

We made similar apparatus with tin wire; the observations with tin in vacuo have, however, not succeeded yet.

§ 16. *Remarks in connection with the experiments with tin and lead.*

α. Our results with tin and lead make it seem probable that all metals, or at least a class of them, if they can be procured sufficiently pure, pass into the super-conducting state when reduced to a low enough temperature. Perhaps in all it would also be suddenly. But the additive admixture-resistance which can be caused by mere traces of admixtures, will in general make the detection of the phenomena a difficult one.

β. A number of experiments with resistance-free conductors

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[1]) It is not possible to solder tin wires into the covers with WOOD-metal: as coming in contact with the tin the melted WOOD-metal, as it seems, penetrates by capillary action amongst the tin crystals which makes the wire brittle and break in two. The tin wires must therefore be melted to the tinned covers, which is possible, by them being provided like the lead wires with sealed on thicker ends.

p. 63 line 11 from the top: after difficulties insert : 3).

of which several suggest themselves at once, now that we can use the easily workable super-conductors tin and lead, can be undertaken with good prospect of success [1]).

In this way the preparing of nonresisting coils of wire, with a great number of windings in a small space, changes from a theoretical possibility into a practical one. We come to new difficulties when we want not only to make a nonresisting coil but to supply it as a magnetic coil with a strong current [2]).

I have been engaged for some time making a preliminary estimation of these difficulties.

The coils mentioned in § 14 and § 15 were made chiefly for this purpose The first of tin wire insulated with picëin, contained on 1 cm. length in a layer of 7 mm. thickness 300 windings of $^1/_{70}$ mm^2. section (the resistance at ordinary temp. was 79 Ω). While a current of 8 amp. could be sent through the wire before it was wound when immersed in liquid helium, without reaching the threshold value of current density (see § 14) the coil came to the threshold value at 1.0 amp. The number of ampere windings per cm^2. of a section through the axis was about 400. The second coil was wound of lead wire of $^1/_{70}$ mm^2. section, and contained in a length of 1 cm. 1000 windings in a layer of 1 cm. thickness. The resistance at ordinary temperature was 773 Ω. The insulation of the wires in each layer was obtained by silk threads, between the different layers a thin piece of silk was placed. I thought that the liquid helium penetrating into the coil through this texture would cause the heat to be given off more easily all over the coil, while it was not certain (comp. the remarks about mercury in glass in § 7 and § 11 Comm VII of this series) that the picëin remained adherent to the tin wire everywhere. Through this coil a current of 0.8 amp.

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[1]) In our first paper about the disappearance of the resistance of mercury we mentioned that this opened a new field of experiment. That mercury is liquid at ordinary temperature was, however, a serious hindrance to entering it.

[2]) A coil of this kind one would wish to place in the interferrum of a very large electromagnet of Weiss, in the same way as the auxiliary coils contemplated by him, in order to further raise the field. The field that is added by the coil would in that case have to be greater than what would be sacrified by enlarging the interferrum to make room for the cooling appliances.

[3]) A possible difficulty was pointed out in note 2 § 4.

(see § 15) could be sent, without the threshold value being reached. The number of ampere windings per cm^2. was then about 800 If the disturbing potential phenomena had not been greater than with the shorter wire of the same section which was washed by liquid helium over its entire surface, and if the difficulty mentioned in note 2 § 4 does not come into play, it would ha been possible to supply this coil with up to 9000 ampere winding per cm^2. If, therefore, the potential phenomena which frustrated this in the experiment reported, in accordance with the opinion expressed in Comm. N^0. VII of this series, particulary in § 11, may be ascribed to "bad places" in the wire, and if we may therefore be confident that they can be removed (for instance by fractionising the wire) and if moreover the magnetic field of the coil itself does not produce any disturbance (note 2 § 4) then this miniature coil may be the prototype of magnetic coils without iron, by which in future much stronger magnetic fields may be realised than are at present reached in the interferrum of the strongest electromagnets [1]).

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[1]) J. PERRIN (Soc. d. phys. 19 Avril 1907) made the suggestion of a field of 100000 gauss being produced over a fairly large space, by coils without iron, cooled in liquid air. CH. FABRY (Journ. d. Phys. Febr. 1910) worked out this idea. He finds that the energy absorbed in such a coil, in watts is represented by the formula

$$W = \rho \eta a H^2 K^{-2}$$

where a is a length in centimetres, which determines the size of the coil, for a cylindrical one the radius of the internal space, η the ratio of the metallic area in a section through the coil at right angles to the windings to the area of this section, K a purely numerical coefficient, which depends upon the form of the coil, and which in cylindrical coils with wire of equal section does not diffe much from 0,18, ρ the specific resistance of the metal of the windings in ohms. centrimetre, H the magnetic field in gauss.

In order to get the desired field of 100000 gauss in a coil with an internal space of 1 cm. radius, with copper as metal, and cooling by liquid air 100 kilowatt would be necessary, putting K at 0,20 and η at 1,5 (which last number might well be 6 times as large). The electric energy supply, as FABRY remarks, would give no real difficulty, but it would arise from the development of JOULE heat in the small volume of the coil to the amount of 25 kilogramme calories per sec. which in order to be carried off by evaporation of liquid air would require about 0,4 litre per second, let us say about 1500 litres per hour.

We may add to FABRY's objection that the preparation of 1 litre of liquid air

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γ. Certainty that the potential phenomena observed are due to such imperfections in the wire would be of no less value for another tempting group of experiments. As soon as the super-conductivity of mercury was established, the question forced itself upon me, in connection with the great value which according to the electron theory of metals is ascribed to the free path of the electrons 1) (comp.

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per hour is at present to be reckoned as requiring not much less than $^1/_2$ K. W. According to this standard, 7 times as much work would be necessary for the cooling than for the current. By a judicious use of the cold of the vapours this number can be reduced, but the proportion will remain unfavourable.

Moreover, as Fabry shows, the dimensions determined by a, to make it possible for the heat to be carried off, would need to be much larger, by which at the same time the amount of liquid gas used becomes greater. The cost of carrying out Perrin's plan even with liquid air might be about comparable to that of building a cruiser!

If we calculate in the same way the cooling with liquid hydrogen in the case of silver and if we assume that the resistance of silver (according to Kamerlingh Onnes and Clay) at the boiling point of hydrogen is 0,009 of that at the ordinary temperature, we arrive at a more favourable figure, namely, that at $a = 1$ cm., 700 liters of liquid hydrogen would be needed per hour, but the ratio of cooling work and electric work becomes more unfavourable yet, putting the preparation of a litre of liquid hydrogen in the same way as above at $1\,^1/_2$ K. W. But the figure for liquid hydrogen would also on the ground mentioned above have to be considerably increased. Although an installation which will give as much liquid hydrogen as is necessary for the cooling could be made after the pattern of the present Leiden plant, it would be of such an extraordinary size that with liquid hydrogen also, the method described perhaps involves more difficulties than a further increase of the size of the coil, in order to be able to cool with running water (as introduced by Weiss) while this method also has its advantages with a view to the use of the field.

The possibility of using the super-conductors tin and lead, gives a new departure to the idea of Perrin of procuring a stronger magnetic field by the use of coils without iron. With super-conductors no Joule heat needs to be carried off (or at any rate only 10^9 times less than with ordinary conductors) and thus with currents below the threshold value the difficulties mentioned above disappear. If the conditions mentioned in the text can be fulfilled, then even a coil of 25 cm. diameter of lead wire, constructed as the one in § 15, immersed in helium, could give a field of 100000 gauss, without perceptible heat being developed in the coil. Some such apparatus could be made at Leiden if a relatively modest financial support were obtained. In the mean time this remark may serve to put the problem of very strong magnetic fields which are becoming indispensable for various investigations in a new form.

1) Comp. note 3 p. 26. Leiden. Comm. No. 119. Febr. 1911.

§ 12 β), whether electrons moving at speeds by which they cannot penetrate a thin plate, e. g. a Lenard's window of solid mercury at the ordinary temperature [1]), or at least not without change of direction, would be able to do this better if the foi were super-conductive. Now that super-conducting plates of tin and lead can be made the experiments on this subject are made practicable, and the plan of making these has assumed a promising form, since I have obtained the prospect of doing it with Lenard himself, which I highly value. If the potential phenomena are caused by local disturbances, we may expect that in experiments with thin plates, by a correct choice of the places to be experimented upon, they will be of little importance. If, as might be imagined according to § 4, the potential phenomena are connected with peculiarities in the movements of the electrons, then they would be of prime importance in phenomena such as we have here under consideration.

δ. The correspondence of the potential phenomena in tin and lead to those in mercury is very striking. As regards tin, it was remarked upon in § 13α, and further investigation has confirmed it and also extented to lead. All the considerations with regard to them for the case of mercury can thus immediately be applied to tin and lead. On the other hand the latter may serve to elucidate the doubtful points in mercury.

With the bare tin wires at 4°.25 K. measurements were made which acquaint us with the amount of heat, given off to the liquid helium above the vanishing point; whether it is proportional to the surface of the wire, as is to be expected, when the heat is mainly given off to the liquid, could not be settled yet. With the rolled out tin wire, with which the various measurements were successful, it was great, which corresponds to the fact that here the ratio between the heat-conveying surface and the heat developed is very favourable. It was estimated at 0.5 watt per 1° difference of temperature. Still at 1°.6 K., 1.4 microwatt caused a local rise of temperature to the vanishing point. As in § 11 we deduce from this that the whole development of heat is local. The hypothesis that in this way „bad places" show themselves

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[1]) Whether the same electron passes through, or whether the movement is carried from the one to the other, does not affect the experimental question.

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p. 66 line 4 from the top: for "at ordinary temperature" read "at temperatures near the ordinary temperature".

line 6 from the bottom: for 1° read 1 degree.

confirmed by the fact that through a wire like this at the
ing point of helium, therefore above the vanishing point,
rrent of 9 amp. could be sent, and all the Joule heat was
bed by the liquid helium, while with a current only a
e stronger the wire gave way (presumably by the forming
nd the wire of a vapour bubble in the helium, which caused
faction in the wire).

The different threshold values for the bare lead wire and the
l coil § 15, and for the bare tin wire and the tin coil § 14, may
ow light upon the influence of more or less easy conditions of
t loss. The phenomena at the disappearance of the resistance
h the bare tin wire with sentinel wires make the hypothesis
owed out in § 12 improbable, namely that the mercury below
vanishing point comes away from the glass or at least does not
e off heat to it at a difference of temperature. The correspon-
nce of the disappearance of the resistance in the tin wire with
tinel wires and in the mercury thread is explained most simply
assuming a local rise of temperature in both, while for both
ow the vanishing point the same opportunity remains for giving off
t, but does not take place owing to absence of rise of temperature.
Here, therefore, the "bad places" mentioned in § 11 (comp. § 12α,
e 1 p. 41) would again remain as the sole explanation. It is
wever suspicious that in the coil of lead wire at 1°.6 K. 56
p./mm². was found as the threshold value, while with lead in
vacuum 270 amp./mm². at 4°.26 K. was reached without a trace
potential phenomena.

Finally we point out that the threshold values of current density
below the vanishing point in the wires of the three different
tals differ very little. We found for the highest limit of the
sible micro-residual resistance determined by the threshold value
proportion to that at the ordinary temperature

$$\text{with mercury } \frac{w_{2^\circ.45\,\mathrm{K.}}}{w_{273^\circ\,\mathrm{K.}}} < 2.10^{-10}$$

$$\text{tin } \frac{w_{1^\circ.8\,\mathrm{K.}}}{w_{273^\circ\,\mathrm{K.}}} < 6.10^{-10}$$

$$\text{lead } \frac{w_{1^\circ.8\,\mathrm{K.}}}{w_{273^\circ\,\mathrm{K.}}} < 0.5\ 10^{-10}$$

In view of so much correspondence and such regularity of the character of all the potential phenomena, it still remains doubtful whether besides the disturbances which we have adduced to explain them, there may not be at the bottom of them peculiarities in the movement of the electrons, which may be more clearly revealed by the experiments indicated in γ.

Having completed the series H of my experiments with liquid helium I wish to express my thank to Mr. G. Holst, assistant at the Physical Laboratory, for the devotion with which he has helped me, and to Mr. G. J. Flim, chief of the technical department of the cryogenic laboratory, and Mr. O. Kesselring, glassblower to the laboratory, for their important help in the arrangement of the experiments and manufacturing of the apparatus.

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COMMUNICATIONS

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PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 134^{a}.

H. KAMERLINGH ONNES, C. DORSMAN and SOPHUS WEBER. Investigation of the viscosity of gases at low temperatures. I. Hydrogen.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, 22 **Maart** 1913, p. 1375—1384).

EDUARD IJDO. — PRINTER — LEIDEN.

Errata Communication N^0. 134.

p. 3 line 5 from the top: for viscotity read viscosity.

I. KAMERLINGH ONNES, C. DORSMAN, and SOPHUS WEBER. *Investigation of the viscosity of gases at low temperatures.* I. *Hydrogen.*

§ 1. *Introduction* 1). The investigation of the dependence of the iscotity of gases upon the temperature at densities near the ormal, is chiefly of importance for the knowledge of the echanism of the impact of two molecules, or, more simply in onatomic gases, of two atoms. In the nature of the case it is esirable to extend this investigation with one substance over the rgest possible range of reduced temperature. This gives a partiular significance to very low temperatures and substances such s hydrogen, neon and helium.

The pupils of DORN 2) at Halle have made systematic researches nto the viscosity of different gases. By these both absolute values nd temperature coefficients have been determined, and they have one as low as the temperature of liquid air.

In our researches we particularly wished to investigate hydroen temperatures, while the viscosity apparatus was so arranged hat it could be used without alteration for helium at helium emperatures. But it was natural for us to extend our investiation to the viscosity of our gases at less low temperatures. It hen appeared that besides being of value for the confirmation of he above mentioned researches as far as the temperature of solid arbonic acid, it was also of value for the knowledge of viscosity n the field of the temperature of liquid air.

In the field of hydrogen temperatures we found the viscosity of

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1) This Comm. includes the paper on the same subject by KAMERLINGH ONNES nd DORSMAN, which is referred to in Comm. Suppl. N⁰ 25. (Sept. 1912) § 6, note 1.

2) There is a survey of these researches by K. SCHMITT. Ann. d. Phys. 30. p. 93, 1909.

hydrogen while flowing through a capillary tube dependent upon the mean pressure. From Maxwell's [1]) researches we know that the viscosity of gases at normal density is independent of the pressure, and Warburg and von Babo have shown in the investigation of carbondioxide, that in dense vapours it increases with the density. There is, therefore, every reason to further investigate the dependence of the viscosity upon the pressure in hydrogen vapour.

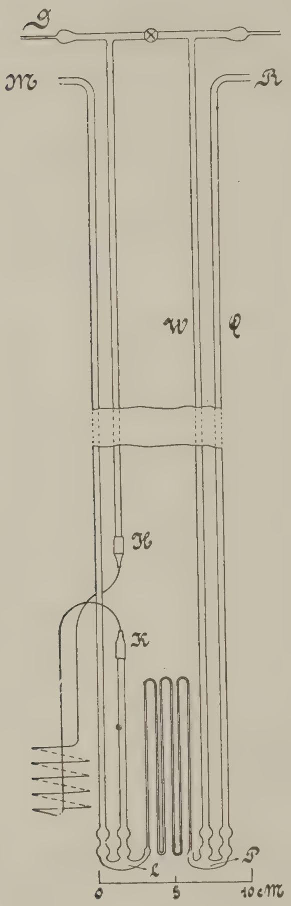

Fig. 1.

§ 2. *Method.* The measurements were made according to the transpiration method. This presents experimentally perhaps the greatest difficulties, but it seems to allow better than any other the fulfilment of the conditions which are assumed in the theoretical deduction.

The form which we chose (diagramatically represented in fig. 1, compare further fig. 2) is distinguished by the following special features:

1⁰. the pressure at both ends of the capillary tube through which the gas flows, can be kept constant as long as desired at any height.

2⁰. the mean pressure and the difference of pressure are immediately measured at both ends of the capillary.

3⁰. before it enters the capillary the gas flows through a copper tube (in our case 70 cm. long) where it acquires the desired temperature.

The calculation of the measurements got by the transpiration method was made by the formulas of O. E. Meyer and

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[1]) For the older literature see H. Kamerlingh Onnes and W. H. Keesom, Leiden Comm. Suppl. N⁰. 23, page 86.

M. KNUDSEN[1]); for the amount of gas that passes through a capillary they give:

$$Q = \frac{\pi}{8} \cdot \frac{1}{\eta} (p_1 - p_2)\, \overline{p}\, \tau \frac{R^4}{L} \left(1 + \frac{4\,\zeta}{R}\right)$$

in which

$$\frac{\zeta}{\lambda} = 1.05 - \frac{1}{5 + \frac{\lambda}{R}} \text{ and } \overline{p}\,\lambda = \sqrt{\frac{\pi}{8}} \cdot \frac{1}{0.30967} \cdot \frac{\eta}{\sqrt{\rho_1}};$$

in this:

η = coefficient of viscosity.

R = radius of the capillary.

L = length of the capillary.

τ = time of flow.

$\overline{p} = \frac{p_1 + p_2}{2}$ = mean pressure.

p_1 = pressure at beginning of capillary.

p_2 = „ „ end of capillary.

Q = the quantity that has flowed through, measured by the product of volume and pressure, and corrected for the temperature of the capillary.

ζ = the gliding coefficient, which is determined by the two last equations, in which ρ_1 is the density of the gas.

The units are those of the *C. G. S.* system.

§ 3. *Arrangement of the apparatus.* The manner in which the various quantities in these formulas were determined in the measurements, will easily be understood with the help of fig. 2.

The pure gas[2]) from a store cylinder is first let into a pipette *P*, in which it can be brought to a suitable pressure by means of mercury. By a high pressure regulating tap it is then con-

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[1]) M. KNUDSEN. Ann. d. Phys. 28. 1909, page 75.

[2]) The gas was purified by passing over a spiral cooled by liquid hydrogen (Comm. N⁰. 83). A trace of air was afterwards found in the gas, this may have been absorbed during the compression in spite of the precautions taken.

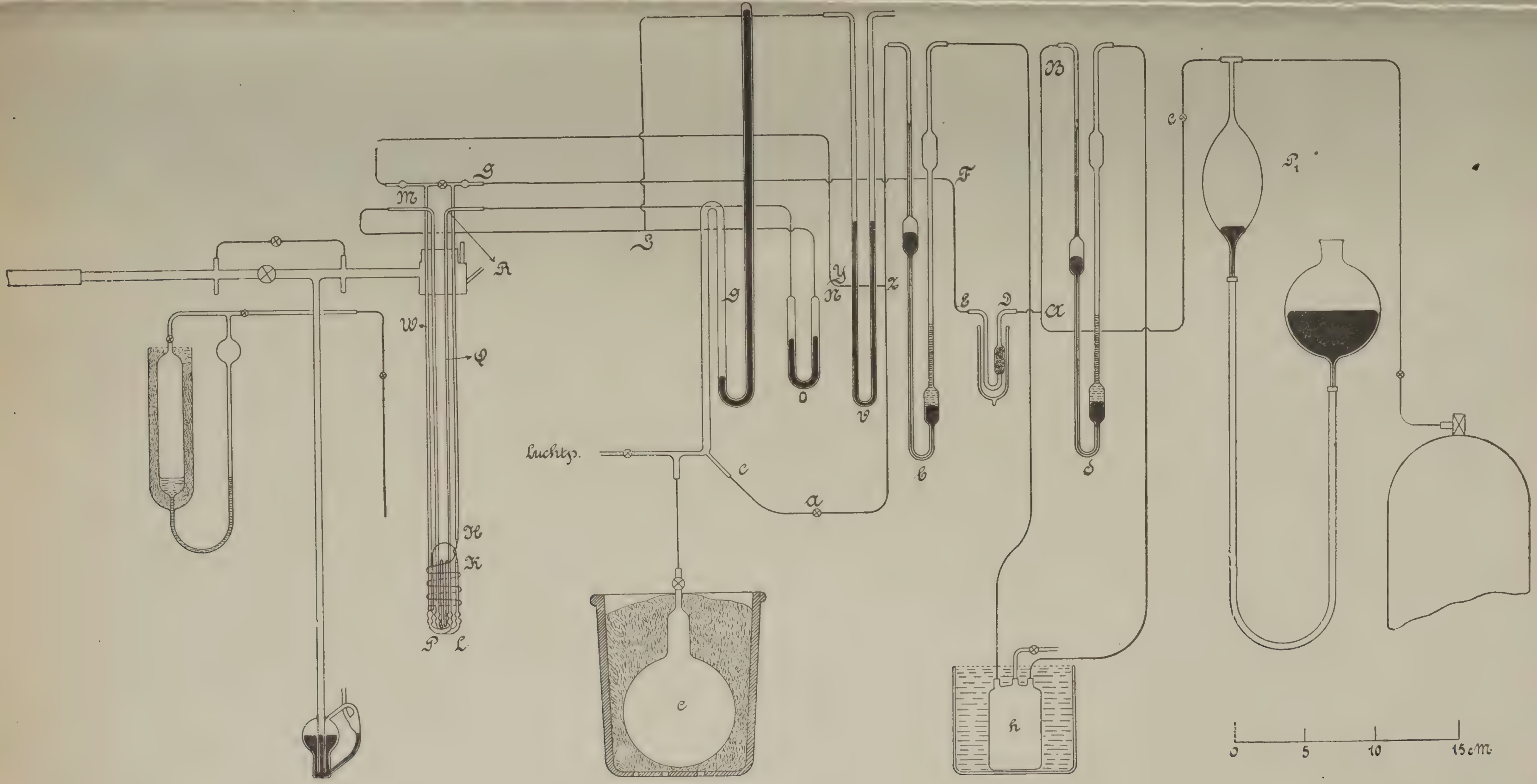
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Fig. 2.

ducted by a brass capillary to A, where the capillary forks. One branch leads to a mercury-water differential manometer, in which the level of the water is kept constant by the regulation of the tap C. At first we worked with oil manometers, which allow an easy adjustment at any pressure required. With these no constant values were found for the viscosity coefficient, which was perhaps in consequence of oil vapour solidifying on the capillary. On this account the oil manometers were replaced by mercury-water differential manometers.

The other branch of the capillary at A leads the gas through a steel capillary EFG to the viscosity apparatus in the cryostat.

Between D and E is a U tube of charcoal immersed in liquid air, by means of which the last possible traces of air would be kept back.

A vertical glass tube carried the gas further. To this was soldered the spiral copper capillary of about 70 cM. length, in which the above mentioned cooling of the gas took place, which had been shown to be indispensible. This terminated at K, from where the gas was carried to L. In L, which was a small reservoir, the tube divides into two branches viz. the capillary and the tube LMN to the mercury manometer O. L and P could be directly connected by a tube in parallel with the capillary and provided with a stop-cock. This was necessary during the exhaustion. The transition from the capillary tube into L, in which the gas may be considered as at rest, is very gradual. This is of importance for the correction of HAGENBACH, which can be omitted in these circumstances. From S a branch $T\,O$ leads further to a second mercury manometer V, which registered the pressure p at the beginning of the capillary tube. Through the capillary tube, (about 65 cM. long, with a diameter of 0,122 mm.) the gas flowed into P. As at L a tube PQR leads from here to the other end of the mercury manometer O. By means of this manometer we could thus read the difference $p_1 - p_2$. Another tube $WMYZ$ leads the gas from P to Z. Z is connected on one side to the mercury-water differential manometer b, and on the other side by a to c. At a there is a regulating tap, which enables us to keep the level of the manometer b at a constant height during the experiment. By doing this during the experiment we can keep $p_1 - p_2$

and p_1 steady, except for the small irregularities due to the regulation of the taps. The tube c is connected to a vessel e of about 4 L. placed in ice, intended for the determination of the volume. The gas pressure in this reservoir was determined before and after every experiment, by reading the manometer g. As can be seen, a small portion of this volume is not reduced to 0° C, it remains at about the temperature of the room. This portion is only about $1.5^0/_0$ of the whole volume.

The three manometers were read by a kathetometer, and were so placed that they could all be viewed by turning the kathetometer.

The temperature of the viscosity capillary was determined by a platinum resistance thermometer placed beside it, which was reduced to the hydrogen thermometer of the Laboratory by comparison with a standard resistance thermometer.

For the arrangement of the cryostat with stirrer see Comm. N^0. 123. The measuring apparatus were immersed in a cryostat glass exactly like that of the helium cryostat. As we said in § 1, it is our intention to determine the viscosity of helium at helium temperature with the same apparatus. The cryostat glass was covered by a cap, which is like that of the helium cryostat, but simplified in an obvious way. In fig. 2 the cryostat glass with stirrer and thermometer are omitted.

§ 4. *Course of the experiments* When the tightness of the apparatus had been properly tested and all found to be in order, the experiment was made in the following way. The volumenometer and the whole apparatus were pumped out and the tap a was closed. Then tap c was opened, and regulated so that the manometers b and d were at the desired height. When this was attained the experiment was begun, and simultaneously with the beginning of the regulation of tap a the knob of a chronometer was pressed. During the experiment, as already said, the taps a and c were so regulated that the differential manometers which acted as indicators, kept constant, at the same time the manometers O and V were read, and the small irregularities which at the most were $1\,^0/_0$, were noted as well as was possible. By the determination of a mean value we find from these readings the pressure difference, which existed between the extremities of the capillary tube during the experiment. If we reduce the readings of the manometer v by $\frac{p_1-p_2}{2}$, we find the mean pressure $\overline{p}$.

The chronometer was compared with the standard clock of the laboratory immediately after pressing the knob. The latter served as the actual time measurer. The end of the experiment was registered in the same way. At the same time tap a was closed. Then the pressure in the volumenometer was read, and herewith the necessary data were obtained.

The distribution of temperature in the cryostat during the evaporation of the bath, may be a source of error, as it affects the distribution of the density in the tubes leading to the capillary tube. These tubes and the time of flow were therefore so chosen that the errors which might arise from this were negligible.

The experiments were usually made at a mean pressure of about $^1/_2$ atmosphere.

RUCKES [1]) has proved that REYNOLDS' criterion applies also to gases. When we determine the critical velocity for our experiments at hydrogen temperatures, we find 3253 cm./sec. while the greatest which occurred in the experiments was 419 cm./sec.

§ 5. *Results.* In the first measurements made with hydrogen in the manner described above, the viscosity became higher and higher, which can be explained by the hydrogen still containing some traces of air which froze in the capillary tube On this account we introduced the tube with charcoal described above. The later determinations gave constant results.

The whole observational material is collected in Table I. The first column contains the temp. in Kelvin degrees, the second and third the difference of pressure and the mean pressure. These results, as already said, are calculated from a great number of observations, the deviations from the mean were about $2\,^0/_{00}$. The fourth column contains the time of flow in seconds, the fifth the increase of pressure in the volumenometer.

This increase of pressure combined with the volume, gives the amount of gas which flows through, and this must be reduced to mean pressure and temperature of the tube through which it flows For this purpose the equation of state was used, which had been deduced from the measurements of KAMERLINGH ONNES and DE HAAS (Comm. N⁰. 127) and KAMERLINGH ONNES and BRAAK (Comm. N⁰. 97*a*).

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[1]) W. RUCKES. Ann. d. Phys. 25, 1908 pag. 983.

The two first observations were used to calibrate the apparatus, in which we assumed with MARKOWSKI ¹) $\eta_{0^\circ} = 841.10^{-7}$, while for C in SUTHERLAND'S formula 83 was taken.

TABLE I

$T°$ K.	$\Delta p_{\text{cm. Hg}}$	$\overline{p}$ cm.Hg	τ_{sec}	$\Delta P_{\text{cm.Hg}}$	$\eta' . 10^7$	$\eta . 10^7$
293.90	11.455	41.83	12739	1.479	"	887.2
293.88	10.750	42.61	16814	1.866	"	
170.2	10.315	43.42	4755.5	1.282	616.8	609.2
170.2	10.310	43.43	6600.5	1.777	617.0	609.4
89.60	6.020	39.47	4760.0	1.999	399.4	392.1
89.65	5.545	40.39	3472.5	1.374	399.4	392.1
89.65	8.485	38.86	3045.0	1.773	399.8	392.5
70.9	6.010	39.48	2610.0	1.711	323.1	316.7
70.9	8.385	38.91	2301.5	2.056	326.2	319.8
70.9	8.300	38.92	1834.0	1.614	327.7	321.3
20.06	4.648	39.08	1264.2	6.565	114.1	111.5
20.04	4.651	39.16	1264.0	6.628	113.5	110.9
20.03	4.630	39.70	1265.5	6.694	113.5	110.9
20.04	3.945	20.40	1684 1	4.021	108.5	106.0
20.04	4.190	19.12	1576.3	3.799	107.0	103 5
20.04	4.580	20.71	1625.0	4.575	108 4	105.9
20.04	4.603	20.37	1357.6	3.787	108.2	107.5

By this means the values were determined which are given under $\eta'.10^7$. They were corrected for the change of R^4/L with the temperature and for the gliding. The corrected values are in column 7 under $\eta.\ 10^7$.

From Table I we can immediately see the degree of accuracy

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¹) H. MARKOWSKI. Ann. d. Phys. 14. 1904. page 742.

that may be ascribed to the measurements with regard to accidental errors. As we have said before the determinations were usually made at a mean pressure of half an atmosphere. At and above oxygen temperatures a determination at one pressure is sufficient, at hydrogen temperatures this appeared to be no longer the case. Table I shows that there the viscosity changes with the density, and in the same direction as was found by WARBURG and BABO for carbondioxide. Our differential manometers were not yet arranged, as we intend to do, for working with different mean pressures, and the apparatus was thus not very suitable for determining the influence of the pressure. In order to perform a few experiments with a different pressure, the two differential manometers were connected to an artificial atmosphere h, as can be seen in the plate.

TABLE II.

$T°$ K.	$\eta_{obs.} \cdot 10^7$	$\eta_s \cdot 10^7$	$\eta_{calc.} \cdot 10^7$
457.3*	1212	1203	1207
373.6*	1046	1050	1052
293.95	—	887.2	886
287.6*	877	874	875
273.0*	844	843	843
261.2*	821	814	816
255.3*	802	800	803
233.2*	760	747	757
212.9*	710	697	709
194.4*	670	648	666
170.2	609.3	582	608
89.63	392.2	326	389
[78.2*	374.2	284	354]
70.87	319.3	257	329
20.04	105—111	58	137

For the further experiments which we intend to make (see § 1) concerning the dependence of the viscosity upon the density, it

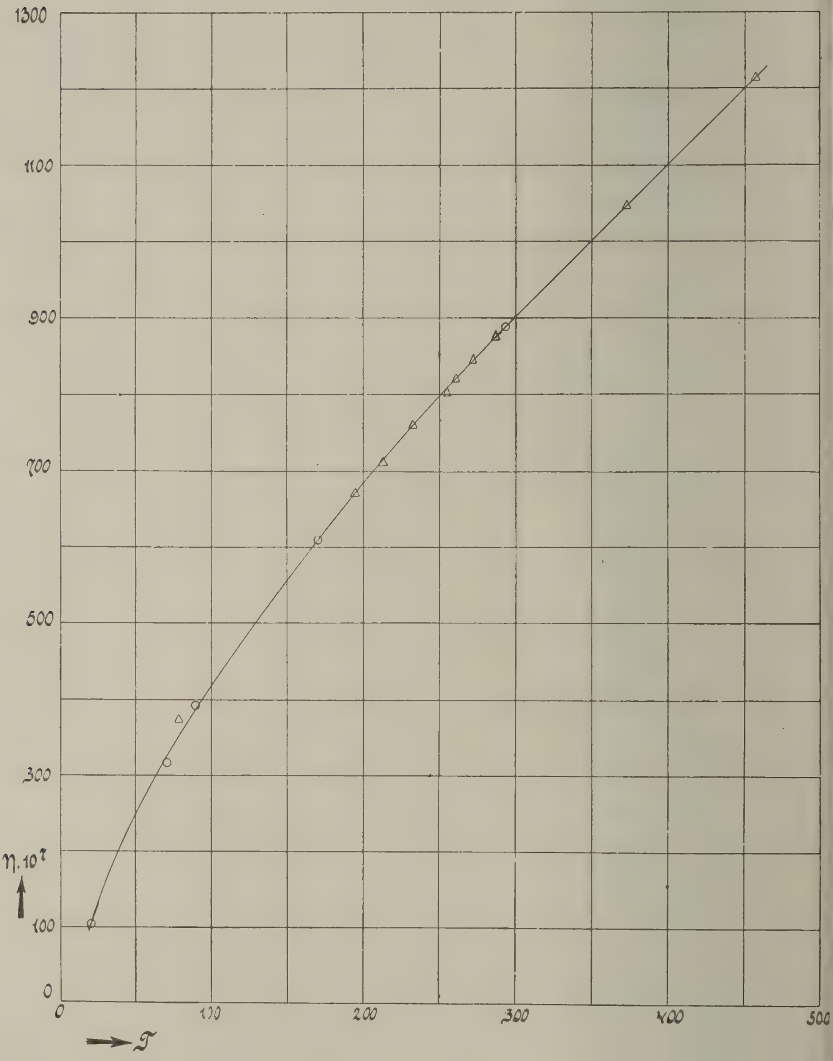

Fig. 3.

may appear that where it is a case of relative determinations only, the oscillation method is perhaps the most suitable.

In Table II our results are put together with those of MAR-

KOWSKI and of KOPSCH [1]) (the last are marked with an asterisk). Fig. 3 shows that our measurements correspond well with previous ones. KOPSCH's determination in liquid air forms an exception. The cause of this is probably an insufficient fore-cooling in KOPSCH's apparatus, as it is improbable that the density should have an important influence [2]) here.

In column 3 under $\eta_s \,.\, 10^7$ are given the values calculated by SUTHERLAND's formula with $\eta_0 = 841.10^7$ and $C = 83$. The differences become very great at the lower temperatures, in liquid hydrogen more than 100 %.

KOPSCH has already pointed out that SUTHERLAND's formula no longer holds for hydrogen at the temperature of liquid air, and although the deviation which he found seems to be partly ascribable to insufficient fore-cooling his conclusion remains correct, as the amount of the deviation of the observations from the formula even at the temperature of liquid air is larger than that of the deviation which is due to insufficient cooling.

We endeavoured to find a simple relation between $\log \eta$ and $\log T$, which would correspond to the observations better than SUTHERLAND's formula. Column 4 under $\eta_{\text{calc.}}\, 10^7$ contains the values of η calculated by the formula.

$$\eta = \eta_0 \left(\frac{T}{273}\right)^{0.695}$$

The correspondence is satisfactory as far as the temperature of reduced oxygen. We shall return to this question in the following paper about the viscosity of helium, in which we shall further deal with the change of the nucleus volume b_w with the temperature, as it follows from our experiments.

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[1]) H. MARKOWSKI loc. cit. en K. SCHMITT loc. cit.

[2]) Observations for He which will be treated in a following paper, show that there is no such dependence on the density.

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No. 134ᵇ.

H. KAMERLINGH ONNES and SOPHUS WEBER. Investigation of the viscosity of gases at low temperatures. II. Helium.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **22 Maart 1913**, p. 1385—1388).

Eduard IJdo — Printer — Leiden.

H. KAMERLINGH ONNES and SOPHUS WEBER. *Investigation of the viscosity of gases at low temperature.* II. *Helium.*

§ 1. *Results.* With the same apparatus as was used for the investigation of the viscosity of hydrogen [1], a series of measurements were made for helium. According to Reynolds the critical velocity would be 2960 cm./sec.; in our experiments the greatest velocity was 105 cm./sec. All our observations are brought together in Table I. The notations are the same as in the previous paper about hydrogen.

Again the first two experiments were used for the calibration

TABLE I.

Viscosity of helium at about normal density, observations and results.

T° K.	$\Delta p_{\text{cm.Hg.}}$	$\bar{p}_{\text{cm.Hg.}}$	$\tau_{\text{sec.}}$	$\Delta P_{\text{cm.Hg}}$	$\eta' . 10^7$	$\eta . 10^7$
294°.50	10,83	36,81	13475	1.565	—	1994
294.55	7.892	44,43	13372	1.370	—	
250.3	9.870	42.98	9540,5	1.539	1806	1788
203.1	8.471	45,65	7828.5	1.622	1591	1564
170.5	8.522	42.60	7191.2	1.851	1420	1392
89.7	10.173	41,07	3201.0	2.709	943.7	917.9
89,8	8,480	44.60	2933.4	2.241	945.6	919.2
75.5	9.744	42.57	1828.1	1.999	841.8	817,6
74.7	7,037	45,30	3220,0	2.810	838.2	813,2
20.17	5,121	41,61	921.1	4.600	362,5	349.9
20.15	5.566	39.49	881.0	4,516	364,6	352,0
20,20	4.540	40.10	846,8	4.540	360.0	347.6
20.16	4.528	11.15	1788.8	2.113	362,9	351.5
20.16	4.530	12,28	1967.2	2.573	362.0	350.7
15.00	3.374	42.73	922.8	5,010	304.1	293.1
15.00	3.962	40,31	821.4	4.921	305.2	294.2
15.00	1.270	41,55	1514 1	2,981	307.5	296.4

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[1] H. Kamerlingh Onnes, C. Dorsman and Sophus Weber. Comm N^0. 134*a*.

of the apparatus, for which purpose we assumed as K. SCHMITT [1]) does, $\eta_0 . 10^7 = 1887$ and C in SUTHERLAND's formula $= 78.2$. In this way we got the values given under $\eta' . 10^7$. These were corrected for the change in $\frac{R^4}{L}$ with the temperature and for the gliding. The corrected values stand in column 7 under $\eta . 10^7$.

As can be seen, most of the measurements were made under a mean pressure of 40 cm. mercury. At 20°.1 K. we also took some measurements at 12 cm mercury pressure. A glance at the table shows that the viscosity does not depend upon the density.

TABLE II.

Viscosity of helium at about normal density and representation of the dependence of the temperature by empirical formulae.

$T°$. K.	$\eta_{obs.} . 10^7$	$\eta_s . 10^7$	$\eta_{calc.} . 10^7$
456.8*	2681	2682	2632
372.9*	2337	2345	2309
294 5	—	1994	1982
291.8*	1980	1979	1970
290.7*	1967	1974	1965
250.3	1788	1771	1783
212.2*	1587	1563	1603
203.1	1564	1513	1558
194.6*	1506	1460	1556
170.5	1392	1317	1389
89.75	918.6	745	918.5
[79.9*	894.7	659	852.1]
75.5	817.6	628	821.3
74.7	813.2	621	815.5
20.17	349.8	135	348.9
15.00	294 6	92	288.7

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[1]) K. SCHMITT. Ann. d. Phys. 30, 1909, page 393.

In Table II our measurements are placed together with those made at Halle by SCHIERLOH and SCHMITT, which are marked with an asterisk. From this and from fig. 1 it can be seen that our results correspond very well with the previous ones. Only SCHMITT's result in liquid air seems to be too high, which perhaps may be explained, as in KOPSCH's experiments with hydrogen, by the gas not being sufficiently cooled before it came into the capillary tube.

§ 2. *Representation of the observations by a formula.* In the same table under $\eta_s \,.\, 10^7$ the values are given which SUTHERLAND's formula gives with the assumed values of η_0 and C. SCHMITT has already found that at the temperature of liquid air a distinct deviation appears. For this observation the same is true as we said about that of KOPSCH with regard to the deviation from SUTHERLAND's formula of the observations on hydrogen at liquid air temperatures.

At hydrogen temperatures SUTHERLAND's formula is shown to be entirely unsuitable for expressing our results. It gives a value two or three times too small. We have tried to represent the series of measurements by another formula, and in column 4 under $\eta_{\text{calc.}} \,.\, 10^7$ we have given the values which we have calculated by the following formula

$$\frac{\eta}{\eta_0} = \left(\frac{T}{273.1}\right)^{0.647}$$

As can be seen, this empirical formula agrees remarkably well with the values found over the whole extensive field of temperatures.

In a following paper we shall discuss the values for

$$\frac{\eta_0}{\eta_t}\,\frac{\sqrt{T}}{\sqrt{T_0}}$$

which follow from our experiments, and further the viscosities at various temperatures for different substances in connection with the law of the corresponding states.

BER. Investigation of the viscosity

PLATE I.

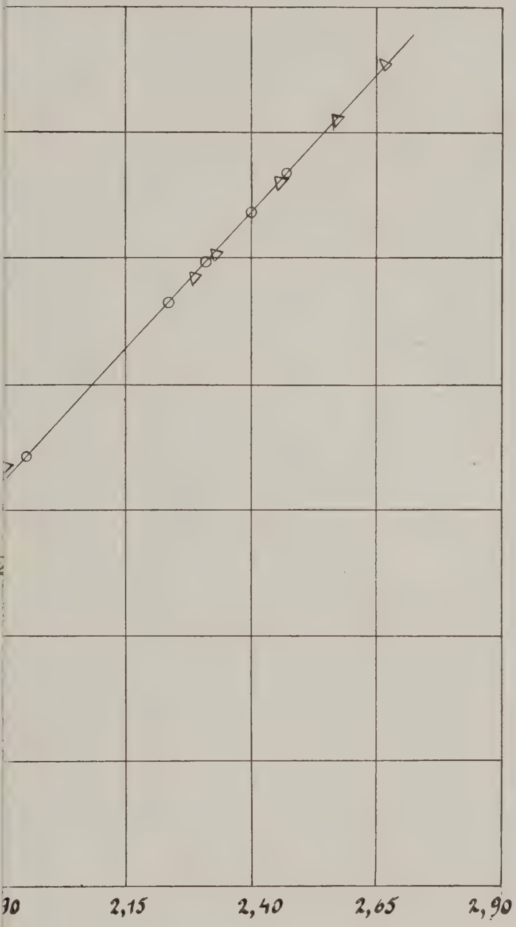

Plate I of

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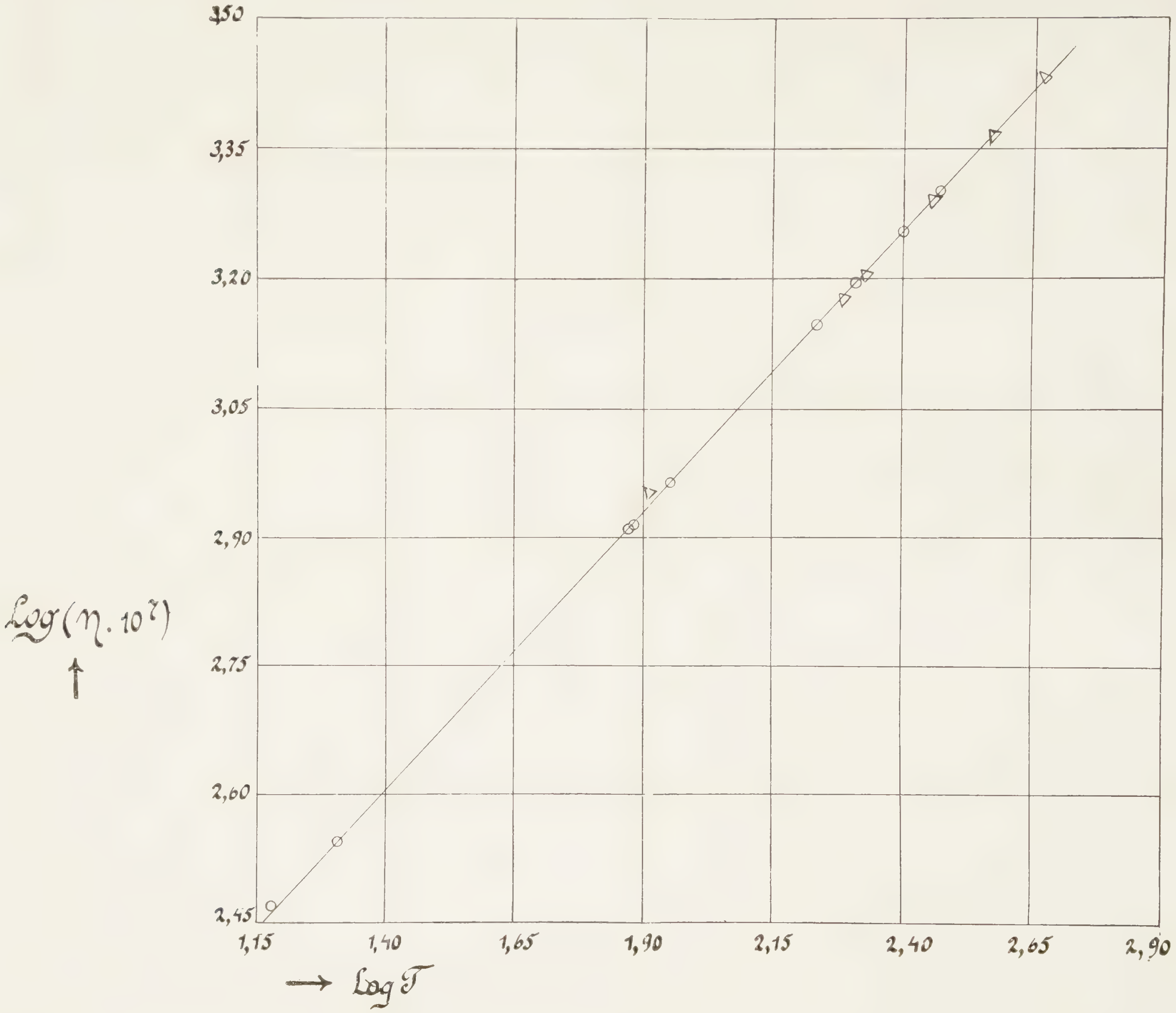
H. KAMERLINGH ONNES and SOPHUS WEBER. Investigation of the viscosity of gases at low temperature. II. Helium. **PLATE I.**



Communication N°. 134^b.

COMMUNICATIONS

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OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

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No. 134^c.

H. KAMERLINGH ONNES and SOPHUS WEBER.
Investigation of the viscosity of gases at low temperatures. III. Comparison of the results obtained with the law of corresponding states.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **25 April 1913**, p. 1530—1534).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and SOPHUS WEBER. *Investigation of the viscosity of gases at low temperatures.* III. *Comparison of the results obtained with the law of corresponding states.*

§ 1. *Dependence of the viscosity upon temperature.* We have already discussed this in our previous papers. It was shown that SUTHERLAND's formula in no way corresponded to the observations at low temperature, either for hydrogen or for helium [1]). REINGANUM'S formula although founded upon acceptable hypotheses about the constitution and mutual action of the molecules, is even worse so long as we regard C in it as constant. This can be easily understood when we consider that SUTHERLAND'S formula can be taken as a first approximation to REINGANUM'S, and that the terms left out must lead to a further divergence from the observations. Neither is it possible to come to an even approximate agreement at low temperature with the empirical correction of REINGANUM'S C which RAPPENECKER has suggested.

We might for instance with helium take $C = C' T \log T$, to come to agreement with the observations. But then REINGANUM'S formula would simply be converted into our interpolation formula.

KEESOM, in Suppl. N⁰. 25 and 26 of these communications has shown, that the second virial coefficient in the equation of state for hydrogen, at temperatures at which this gas may be regarded as di-atomical, can be very satisfactorily explained by the supposition that hydrogen molecules are hard spheres with electric doublets in the centre. His formula for the virial of the collisional forces under these circumstances gives a change of the radius of the molecule with the temperature, which for higher temperatures agrees fairly well with that deduced from the viscosity by $\frac{\eta_t \sqrt{T_0}}{\eta_0 \sqrt{T}}$. At lower temperatures at which hydrogen behaves like a monatomic gas, the formula for hard spheres with a central force according to the law r^{-q} becomes applicable, and Keesom finds this again confirmed by the change of the viscosity with the temperature.

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[1]) Shortly after our paper an important article by EUCKEN appeared in the Phys. Zeitschrift (April 15th 1913) in which observations concerning the viscosity of helium and hydrogen taken from an as yet unpublished paper by VOGEL were communicated. Within the limits of accuracy, which in VOGEL's observations are given at 5% at hydrogen temperature, these confirm our measurements, of which the accuracy at hydrogen temperatures is to be put at about 1%.

But when we go down to —193° C. deviations appear, in accordance with what we said above about Sutherland's formula, and at lower temperatures the value of the viscosity becomes much too small.

None of the formulas deduced from theoretical suppositions can represent the observations for helium; for the present we can only use our empirical representation for this substance, which for hydrogen also holds good for lower temparatures than the theoretical formulas, viz. as far as the temperature of reduced oxygen. As regards the formula for helium, it is not impossible, that the straight line in the logarithmic diagram must be replaced by one that at low temperatures, and perhaps at higher ones also, curves somewhat towards greater values of the viscosity.

§ 2. *Application of the principle of mechanical similarity upon the comparison of the viscosities in corresponding states.*

If two substances may be taken as mechanically similar systems of molecules, it follows 1) that the viscosities for both in correponding conditions must be in a constant ratio which may be calculated from the ratios of the units of length, time and mass in both systems. On the other hand from the values of

$$-\frac{1}{2}\log\frac{\eta}{\sqrt{T}\sqrt{M}} = \log\sigma - \log c$$

where M is the molecular weight, σ the mean radius of a molecule, as it is effective in viscosity, and c a constant, the same for all substances, we may, when the curves which express the connection between η and $\frac{T}{T_k}$ are the same, infer the ratio between

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1) H. Kamerlingh Onnes. Verh. Kon. Akad. Amsterdam 21, p. 22. 1881 Beibl. 5. p. 718. 1881.

p. 25 line 13 from the top: for $M^{-1/2}\ T_k^{-1/6}\ p_k^{2/3}$ read
$M^{1/2}\ T_k^{-1/6}\ p_k^{2/3}$.
line 11 from the bottom: for followings read following.

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the units of length which have to be ascribed to the two mechanically similar [1]) systems. With the help of the viscosity we can, therefore, make a comparison of the just defined mean molecular radii and we may inquire how far the ratio found corresponds to that of the mean molecular radii, determined in the way that is necessary in the deduction of the equation of state. If this correspondence were complete, then, when the expression of σ given above is expressed in reduced quantities, the curves which express the logarithm of the reduced σ as a function of the logarithm of the reduced temperature for the various substances, would coincide The accompanying diagram shows in how far this is the case. In the construction $M^{-1/2}\ T_k^{-1/6}\ p_k^{2/3}$ has been used as the ratio by which the viscosities [2]) are reduced to the same imaginary system. In this we have taken p_k and T_k which hold for the critical state [3]), as determining quantities, and postponed the consideration of deviation functions till later [4]).

The first thing that strikes one is the great deviation of helium. In § 1 we remarked that the character of the viscosity of helium can be expressed by replacing the constant c, which may be understood as a measure for the attraction between the molecules, in Reinganum's formula (differing by a constant factor from υ in Keesom's formula) by $c'\ T \log T$. Perhaps this points to an increase with the temperature of the quantity which determines

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[1]) More correctly: mechanically and statistically similar.

[2]) H. Kamerlingh Onnes. Leiden Comm. N°. 12, p. 9.

[3]) The critical data we have used are the followings.

	p_k (Atm.)	T_k
H_2	15.0	32.0° K.
He	2.26	5.25
O_2	50.0	155.0
N_2	33.0	127.1
Ar	48.0	150.7
CO	35.9	132.0 [Note added in the translation.]

[4]) Kamerlingh Onnes and Keesom Suppl. N°. 23, Nr. 38. The ratios found by Keesom in Suppl. N°. 25 p. 12. note 3, give 6 % deviation for hydrogen and argon, those used here 9 %.

the attraction of helium. KAMERLINGH ONNES was also led to assume a similar increase of the attraction with the temperature, to explain peculiarities in liquid helium, and KEESOM in discussing the second virial coefficient of helium at higher temperatures, found that peculiarities of this coefficient might be ascribed to the same cause; in this case the receding of the attraction sphere (or the greater receding than in other substances) might be the cause of a slighter decrease of the viscosity at the reduction to lower temperatures. There might, however, also be an expansion of the molecule (in this case the atom) with temperature, and finally both phenomena might be dependent upon one cause, and go together. The possible small curvature for helium of the line in the logarithmic diagram [that we mentioned in § 1] in the opposite sense to that of the other lines which expresses the difference between helium and other substances, could be ascribed to this change in the attraction.

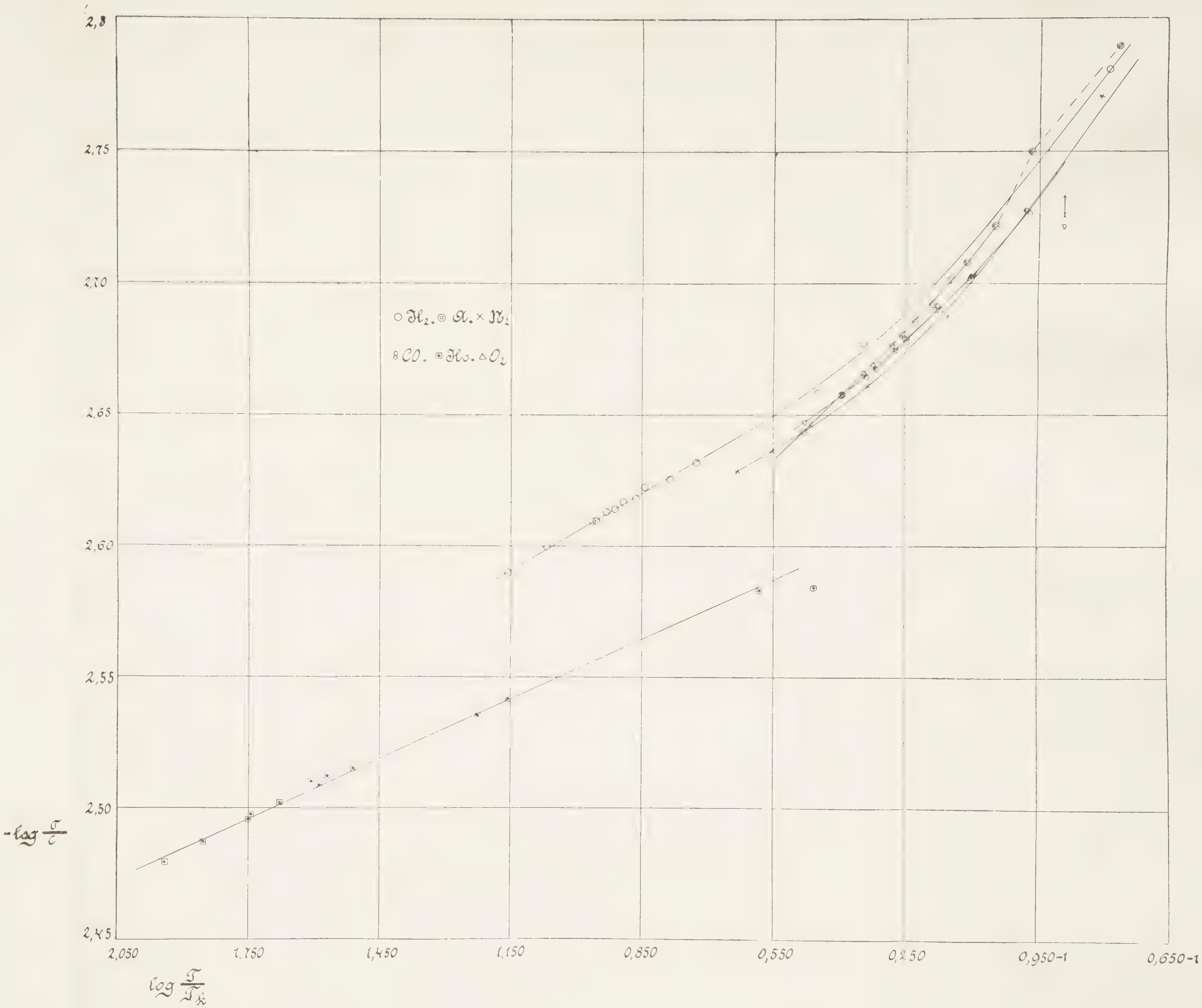
That which might explain the deviation for helium of the slope of the line from that which holds for a large range of temperatures for other substances, may also possibly help to explain the deviation from REINGANUM'S formula at low temperatures, by the quantity which determines the attraction becoming smaller.

With hydrogen at the temperature of liquid air there is a distinct change in the slope of the curve. It is remarkable that the same is found with nitrogen, and perhaps also with oxygen and carbon monoxide, and that the point at which it occurs seems to lie at the same reduced temperature for hydrogen and nitrogen and perhaps also for oxygen and carbon monoxide. If this is the case, then the change which in the hydrogen molecules may according to KEESOM be taken as a change from hard spheres with electric doublets into hard spheres with a central force r^{-q} as far as concerns the viscosity, would be a similar process for all these different substances, determined by the same units of length, time and mass as hold for the critical quantities, while this point only coincides with the point of transition in the specific heat of diatomic substances in the special case of hydrogen.

We must further notice the systematic differences between the different substances which appear from the non-coincidence of the curves. It is remarkable that most of them (except a part of argon) can be removed by shifting the curves. The mean value of the molecular radius which comes into consideration for the viscosity, seems thus to differ from the mean value which comes into consideration for the equation of state at the critical temperature, but both are in a fixed relation for the various materials over the whole field of temperature. This might be ascribed for instance, to a more elongated shape of the molecules in substances which give the smallest viscosity.

H. KAMERLINGH ONNES and SOPHUS WEBER. Investigation of the viscosity of gases at low temperatures. III. Comparison of the results obtained with the law of corresponding states.

PLATE I.



Communications No. 134c.

COMMUNICATIONS

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BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 134^d.

H. KAMERLINGH ONNES and E. OOSTERHUIS. Magnetic Researches. VIII. On the susceptibility of gaseous oxygen at low temperatures.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **25 April 1913**, p 1535—1537.)

EDUARD IJDO. — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and E. OOSTERHUIS. *Magnetic Researches.* VIII. *On the susceptibility of gaseous oxygen at low temperatures.*

§ 1. *The susceptibility of compressed oxygen between* 17° C. *and temperatures near the critical temperature of oxygen.* In our last paper in connection with our investigations of various cases in which a molecular field of WEISS with opposite sign can be assumed with paramagnetic substances, we mentioned the continuation of the experiments by KAMERLINGH ONNES and PERRIER which have already been projected and the continuation of which may soon be expected, and which have for their object, to investigate the influence, with oxygen, of bringing the molecules to various densities upon the deviations from CURIE's law. Working in the same direction, we have endeavoured to ascertain whether in gaseous oxygen below the ordinary temperature and above the critical temperature a Δ appears. For this purpose we have measured the susceptibility of oxygen between 17° C. and —126°.7 C. We used the attraction method in the same form as described for the paramagnetic salts in our previous paper. A copper tube, closed underneath, 10 cm. long, 8 mm. external and 6 mm. internal diameter, provided with a capillary tube above, by which it could be filled with oxygen under pressure, and closed, one time with a fine tap in which the capillary tube ended, another time by pinching this capillary, and then soldering up after it had served for filling, was filled with oxygen at ordinary temperature to 100 atmospheres. The experiment was then repeated with the evacuated tube in the same baths. For results: see table I.

The experiments should be regarded as comparative for the question under consideration, but the absolute value of the susceptibility was also determined at 289°.9 K. It corresponds pretty well to that of WEISS and PICCARD. As manometer we used a metal manometer which was compared with a hydrogen manometer going to 120 atmospheres. The density of oxygen was taken from AMAGAT. χT appears to be constant, within the limits of accuracy (which is about 1 %) as far as the boiling-point of ethylene (169°.6 K). The two points in ethylene, evaporating under reduced pressure, deviate a little, but this need not be considered as of much importance, as these temperatures were not accurately known. Moreover the proximity of the critical temperature made the distribution of density in the tube uncertain.

TABLE I.

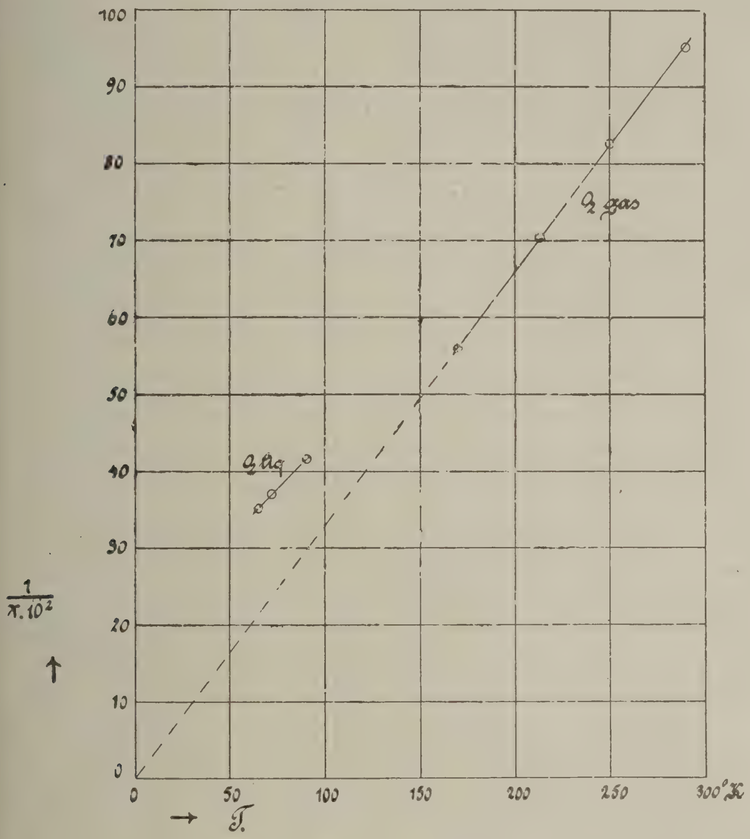
Gaseous oxygen ($\rho_N = 100$)

$H = 10$ to 18 Kilogauss.

T	$\chi \cdot 10^6$	$\chi \cdot T \cdot 10^4$	Bath.
289°.9 K.	105	304	In air.
249 7	121	302	Liquid methyl chloride.
212.1	142	301	
169.6	179	304	Liquid ethylene.
[157.7	188	296]	
[146.6	201	295]	

We may draw the conclusion that within the limits of accuracy in the measurements a Δ does not yet appear in oxygen above the critical temperature at densities which are 100 times the normal. From this it seems all the more probable that Δ only appears for oxygen at great densities, and in liquid oxygen can rise to the considerable value of 71° as the density rises to 1000 times the normal.

In the accompanying figure our observations concerning gaseous oxygen and those of KAMERLINGH ONNES and PERRIER which we confirmed in our last paper, are combined in a graphic representation; the uncertain points near the critical temperature are not given. The point of intersection of the line for gaseous oxygen with the production of the line for the liquid state, appears to have no physical meaning; as we supposed in our last paper, it is due to the value of the constants, that the temperature which indicates the intersection of these lines happens to be about the



ordinary one, at which amongst others, the observations of PICCARD and WEISS fall, and below which as yet no observation had been made for gaseous oxygen. *(To be continued.)*

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H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 135.

Madame P. CURIE and H. KAMERLINGH ONNES.

The radiation of Radium at the temperature of liquid hydrogen.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **25 April 1913**, p. 1537—1549).

EDUARD IJDO — PRINTER — LEIDEN.

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Madame P. CURIE and H. KAMERLINGH ONNES. *The radiation of Radium at the temperature of liquid hydrogen.*

One of the most remarkable peculiarities of radio-active substances, is that the radiation is independent of the temperature. Neither do the radio-active constants change with the temperature. These two facts are related to each other; they prove that the radio-active transformations are not affected by the influence of temperature, which plays such an important part in the chemical transformation of the molecules.

According to the theory of radio-active transformations, the intensity of radiation of a simple substance is proportional to the rapidity of the transformation, so that a change in one of these quantities involves a change in the other.

The experimental investigations of the influence of temperature have been concerned with the measurement of the radio-active constants and the intensity of radiation of certain substances. P. CURIE has shown that the law of transformation for the emanation does not change at a temperature of 450° C. nor at the temperature of liquid air [1]). Various observers have proved that the penetrating radiation of radium and uranium have the same value at ordinary temperature and at the temperature of liquid air [2]). The influence of high temperatures on the radium emanation and its transformation products, particularly Radium C, has also been the subject of various investigations. The results have given rise to differences of opinion. Nevertheless it would seem to be justifiable to conclude that the dependence upon temperature which was observed in some cases must be attributed to secondary phenomena of less importance, and that the radio-active constants of the above substances are not appreciably altered when the temperature is raised to 1500°[1]).

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[1]) P. CURIE, C. R. 1903.

[2]) BECQUEREL, CURIE, DEWAR, RUTHERFORD.

As the question is of great importance it was desirable to enlarge the results already obtained, by extending the experiments over a wider range of temperature and by increasing the accuracy of the measurements, which in the above mentioned investigations could not have been greater than 1 °/₀ at the most.

Our object was to descend to the temperature of liquid hydrogen. By using a compensation method we were able to determine very slight changes in the radiation intensity. Our measurements were concerned with the penetrating radiation of radium. The results, within the limits of accuracy which may be placed at 0.1 °/₀, do not confirm the existence of a quickly acting influence upon the radiation, in consequence of this strong decrease of temperature.

The investigations were made in the first part of 1911. The preliminary measurements were partly made in Paris, and partly in Leiden, while the final measurements took place in Leiden in July 1911. We intend to continue and extend the experiments, which is the reason of the publication having been postponed. But as the continuation of the work has been prevented so far by the long indisposition of one of us, we thought it best not to wait any longer in publishing our results.

Apparatus and arrangement of the measurements. After some preparatory experiments we decided to use the following apparatus. The apparatus consists of a vacuum glass A, in which a copper vessel B is placed, which contains the low temperature bath. The vacuum glass, which is fairly wide at the top (a_1) consists underneath of a tube-shaped portion, the length of which is about 16 cM. and the two diameters 8.5 and 13 mm. The copper vessel which fits into the vacuum glass, is also provided with a tube-shaped portion, which is shorter than that of the vacuum glass. This copper tube is closed underneath (B_1) by a

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[1]) Curie and Danne, C. R. 1904. Brown, Phil. Mag. 1906. Makower and Russ, Le Radium, 1907. Engler, Ann. d. Phys. 1908. Schmidt, Phys. Zeitschr. 1908.

Errata Communication N⁰. 135.

p. 4 line 3 from the bottom: for BROWN read BRONSON.

metal stopper C_1, to which a tube C_2 of thin aluminium is atta-

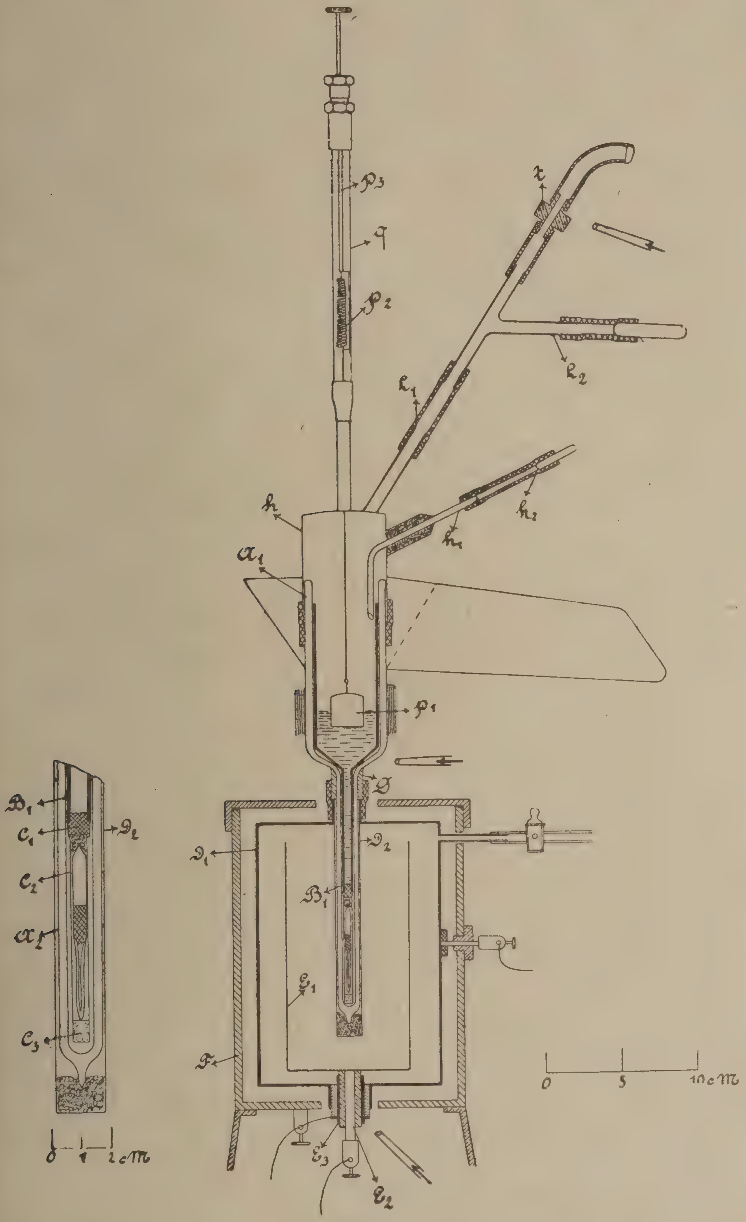


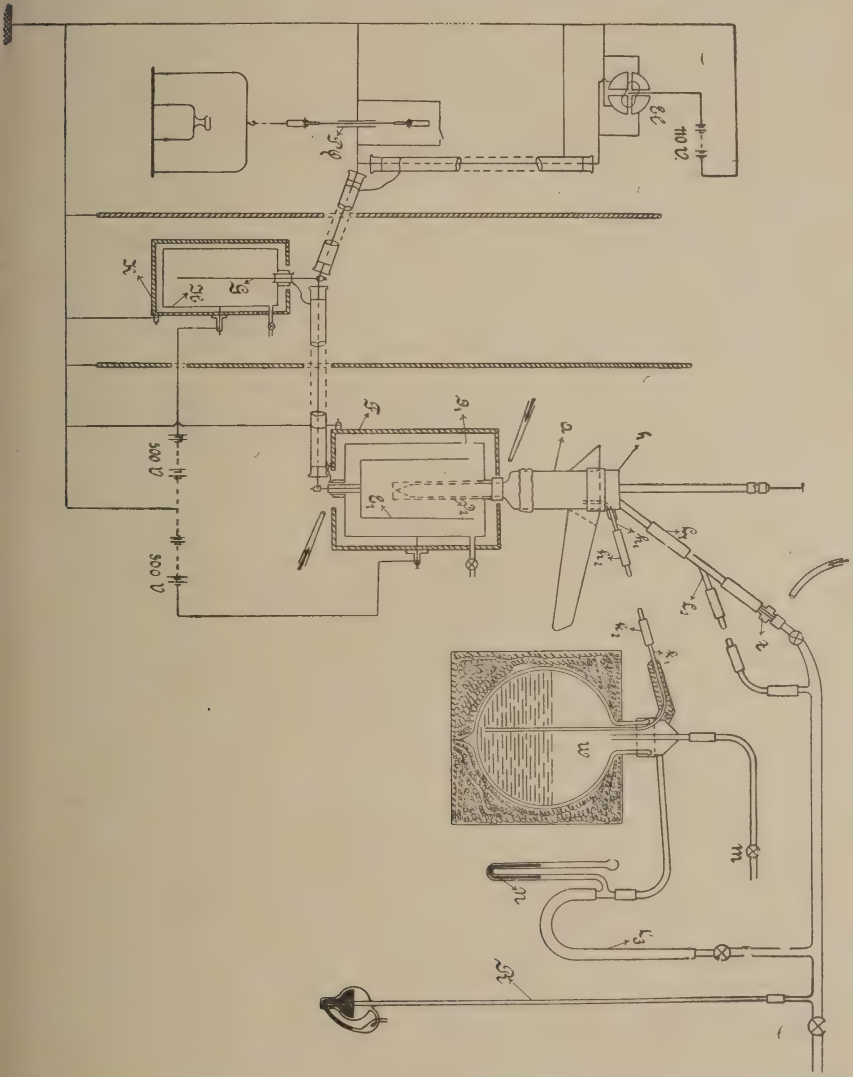
Fig. 1.

ched (thickness 0.3 mm.); this tube contains a sealed glass tube with the radium. The narrow space at the bottom of the vacuum glass in which this tube is placed, is cooled to a temperature that differs very little from that of the bath: the difference could hardly be established, when the copper vessel was filled with liquid air. This method of cooling seemed to us to be preferable to placing the tube itself into liquid gas, which is always a little dangerous.

The rays that the radium in the tube sends out are partly of a penetrating nature. They go through the walls of the aluminium tube and those of the vacuum glass, and penetrate through a metal wall into the ionisation space. This consists of a cylindrical box D_1, which is connected to a battery; in the middle of the lid of this space a tube is soldered, which is closed at the lower end. The insulated electrode E_1 which is a hollow cylinder, is connected with the electrometer. The metal case F, which is connected to earth, serves for electrostatic protection. When the apparatus is mounted the tube shaped portion of the vacuum glass is inside the tube D_2, which is placed centrally in the box D_1, while it is closed by a thick piece of india-rubber tubing round a piece of amber G which is sealed to the vacuum glass. When the tube containing the radium is in its place, ions are formed on both sides of the electrode E, in the air that fills the box D_1. The current that is taken up by this electrode is measured by an electrometer and a plate of piezoquartz.

The experiment consists in measuring the ionisation current generated by the rays of the radium: 1⁰. when the radium is at the temperature of the room, and 2⁰. when the radium is cooled to the temperature of liquid hydrogen. The ionisation chamber, which is outside the vacuum glass remains at about the temperature of the room. The chamber is airtight, and the quantity of gas that it contains does not alter during the experiments.

The accuracy of the measurements is greatly increased if instead of measuring the total current, a compensation method is used. This consists in compensating the current to be measured by a current in the opposite direction, which is generated in a second ionisation chamber by a tube containing radium, which is kept at constant temperature during the experiments. This current compensator is of a type which is greatly made use of in radioactive measurements. The insulated electrode G is in the form of a tube which is closed at the bottom; it is connected by means of copper wires (electrically protected in brass tubes filled with paraffin wax) with the electrometer and with the electrode E_1.



This tube reaches into a cylindrical box H_1 which is connected to a battery and which forms an ionisation chamber. The outside case K serves for electrostatic protection. The electrodes G and E_1 are protected in the usual way by a protecting ring connected to earth. The tube G contains a sealed glass tube with radium salt. The boxes D_1 and H are kept at high potentials of opposite sign. Under these circumstances the difference of the two ionisation currents is measured which are generated in the two chambers With sufficiently strong currents great accuracy can be attained in this way.

It is worth noticing, that the various small imperfections in the method of measuring, which are usually unnoticed, become apparent when the method above described is pursued. For instance, when each current is measured separately, the saturation appears to be complete at a potential of about 500 volts. But when the difference between the currents was measured, which was usually under 5 % of each current separately, it was found that the current under these circumstances increased with the voltage. When the potential increases from 500 to 800 volts, the current increases by 2 to 3 thousandths. Constant potentials must therefore be used.

The accuracy is limited by the stability of the apparatus and by the oscillations in the radio-active radiation.

The investigations were made with radium salts in the solid state, contained in sealed glass tubes; the salt was finely granular, and the tubes were not quite filled. When they are shaken the grains can move to a certain extent, which causes a slight change in the distribution of the radiation inside the ionisation chamber. The danger of this is lessened by giving the grains a definite arrangement beforehand by tapping the tube. But in spite of this, small perturbations of this nature remained in our experiments of not more than 1 in 1000. The very greatest care is, therefore, necessary in the manipulations which must be made during the experiments.

The radio-active oscillations of the ionisation current become apparent when the sensitivity of the measurements is raised sufficiently. They cause irregular deviations which can only be eliminated by a great number of measurements. They are least to be feared when gamma rays are used, as was the case in our experiments. In our case they could not do any harm to the determinations.

It is important that the ionisation chambers should contain an unchangeable quantity of air. When working with penetrating rays, the current is approximately proportional to the amount of ionised air. If one wishes to keep the current constant with great accuracy, we must, therefore, take care that the ionisation chambers are properly closed. Each chamber is supplied with a tap. By changing the amount of air in the compensation chamber, the current in the chamber could be so regulated as to get a compensation of the amount required. Both the compensation chambers are filled with dry air by a tube filled with cotton wool, which can be connected to the tap of the chambers by a ground joint, and to an air pump and a manometer to regulate the supply.

We had to take very great precautions to prevent the cryogene operations from causing insulation errors in consequence of the precipitation of moisture from the surrounding air on the strongly cooled parts of the apparatus. The cryogene apparatus used by us enabled us to avoid all difficulties of this sort. This instrument, which was arranged for working easily and safely with liquid hydrogen, had moreover the advantage that the radium tube could only come into contact with the gaseous phase of the liquified gas, so that when this was hydrogen there was no fear of solid air being deposited on the tube.

The cryogene apparatus is completely closed. The vacuum glass has a lid h of thin new silver, which is fastened air tight to the glass by means of an indiarubber ring, so that when the radium tube is in its place, the apparatus can be evacuated, and can be filled beforehand with pure, dry gaseous hydrogen (by L). A small hole in the stopper C_2, upon which the radium tube in the aluminium tube rests, ensures the pressure equilibrium, which establishes itself easily during these operations, so that the radium tube is not exposed to any danger.

The liquid hydrogen is poured into the vessel B through the new silver tube h_1 and through the india-rubber tube h_2. For this purpose the glass stopper is removed which closes the india-rubber tube, after the tube with the stopper K_2 has also been taken away, and the india-rubber tube is connected to the syphon K_1 of the large vacuum glass W, containing the liquid hydrogen that has been previously prepared. Before the syphon and the indiarubber tube are connected, the apparatus and the vacuum glass are connected to a gasometer with pure hydrogen, by the tubes L_1 and L_2. When the first mentioned connection has been made, the connection of the vacuum glass with the gasometer is broken, and the liquid hydrogen is poured into the apparatus by means of pressure from a cylinder with compressed hydrogen, admitted by the cork m, and controlled by the mercury manometer n. The supply-glass and the gasometer are then again connected. The syphon is taken off the inlet tube after the connection tube has been warmed, and this last tube is immediately closed by a glass stopper.

To prevent these manipulations from shaking the apparatus, we made the indiarubber tube h_2, which is usually as short as possible, rather long; but as the great cold makes the india-rubber very brittle, and the breaking of it might cause great inconvenience, we used only a length of 7 c.m. In this way the shaking remained below the limits of stability in the apparatus which we used for these experiments. In a larger apparatus, intended for experiments that take longer, more than 24 hours, but with which we have only been able to make preliminary determinations so far, we were able to attain a greater amount of stability, and we were more independent of the shaking caused by the manipulations.

Care must be taken in filling the copper vessel B, that the liquid gas does not overflow, as it might penetrate into the cooling chamber, which would give rise to irregularities, and might injure the radium tube. On the other hand it is necessary to know when the liquid gas has evaporated, otherwise the experiments might be continued without being certain of the temperature. The height of the surface of the liquid gas can be read by means of a float. This consists of a new-silver box p_1, suspended from a weak spring p_2, which spring is attached to a rod p_3. This rod is movable in a packing tube, which is fastened to the upper end of a glass tube q, carried by the lid h. Beside the spring, and also hanging from the rod, is a flat rod which is provided with a scale at its lower end. In consideration of the very small density of the liquid hydrogen ($^1/_{14}$), the float is made very light. When the float reaches the surface of the liquid by the moving down of the spring, this is indicated by the shortening of the spring, and he height of the liquid can be read on the scale and on the rod.

Before pouring in the liquid gas, the float is regulated to the eight to which the vessel is to be filled. Before beginning the neasurements, the spring is pressed down as far as is necessary o make the lengthening of it show when the liquid is so far vaporated that the measurements must be stopped.

The evaporated hydrogen is carried off by L_1. The tube R, he extremity of which is placed in mercury, serves as a safety.

In order to be certain of the insulation of the vacuum glass, and o avoid currents that might be injurious to the constancy of the ension of the battery, a piece of amber is interposed in the tube L_1. To prevent the amber being cooled too much by the filling, he cold vapours are carried off by a supplementary tube L_2, which is coupled off as soon as the filling is completed. When he evaporation of the bath has become stationary, a current of ir a little warmer than that of the room directed upon the amber is ufficient to maintain the insulation. This current of air is given y a reservoir of compressed air, the air flows through a long ube part of which is warmed by hot water.

The connection of the amber g_1 which is sealed to the vacuum glass, with the tube D_2 of the principal ionisation chamber, is very carefully made, to insure an air tight closing, and thereby o prevent the possibility of moisture penetrating to the space etween the tube and the vacuum glass. The currents of cold air hat come down are kept away by a paper screen. The water that runs down the glass from the lid must also be disposed of. The very low temperature of the vapours inside the lid causes frost o settle on it during the filling, which thaws afterwards. After he filling is finished, the condensation of water vapour out of the air continues; the water thus formed, is absorbed by cotton wool above the paper screen we mentioned, and below it by filter-paper. A current of dry slightly warmed air is directed upon the amber, which at the same time dries the lower part of the vacuum glass.

Finally, the cooling of the parts of the connection of the main electrode E_1 with the electrometer must be prevented. To ttain this a current of dry and slightly warmed air is also directed upon the amber stopper between the stem E_2, and the protecting ring E_3 at the bottom of the main ionisation chamber.

The cold currents of air, which come down from the tubes that lead off the gases, are diverted from the apparatus by suitable screens, and large currents of air in the room are avoided as far as possible, so as to prevent the ionised air around the contacts from being displaced; these contacts were further protected by various lead protecting mantles (in the figure diagrammatically represented), by tin foil, etc. The influence of the warm currents of air already mentioned was tested at the temperature of the room: they did not cause any electrostatic phenomena.

Preparatory Experiments.

The experimental method was first studied in Paris, using liquid air as cooling bath.

The current in the main ionisation chamber was procured by using a tube with about 0.1 gr. of radium chloride. In the compensation chamber a tube with about 25 mgr. of radium chloride was used.

In the first experiments the first tube was contained in an aluminium tube with walls of 0.3 mm. thickness; the central tube D_2 in the chamber D_1 was also of aluminium, with walls of 0.5 mm. thickness. The rays, before penetrating into the ionisation chamber, passed through a layer of aluminium of about 0.8 mm. and moreover a glass thickness of about 2.5 mm. (wall of the radium tube and both walls of the vacuum glass).

During the cooling a diminution of the current in the main chamber could be observed. It was not very regular, and was about 2 %₀, it was perceptible immediately the liquid air was poured into the copper vessel, and reached its maximum in abou half an hour.

When, however, the liquid air was quickly taken out of the vessel, and the temperature of the radium tube followed with a thermoelement, it could be observed that while the temperature of the radium tube was still constant, the strength of curren already began to rise, and reached about its original value, by the time the whole apparatus had returned to ordinary temperature From this it was evident that decrease of strength of curren which we observed, was not attributable to a change of radiation n the radium tube, but to some other cause.

Various test experiments seemed to show that it was caused y a change in the power of absorption of the screens, due to heir contraction at low temperatures. It was therefore necessary o make use of heavier and thicker screens, to make sure that we only worked with the most penetrating rays, which are less usceptible to phenomena of this kind. After the radium tube ad been inclosed in a copper tube of 1 mm. thickness, we ound that the decrease of current when the liquid air was oured in was reduced to 0.1 °/₀. The decrease was completed in 0 minutes. Three successive experiments gave this result.

We found that we could make the circumstances even more avourable, by changing the arrangement of the apparatus in uch a way that the screens in which the absorption of the ays took place were not cooled at all. In order to do this, the adium tube was once more put into the aluminium tube of 0.3 m., while the central tube D_2 of the chamber D_1 was replaced y a brass tube of 2 mm. wall thickness. The decrease of the urrent became by this means less than 1 in 1000. This arranement was used in the final experiments.

Final Experiments.

The experiments were made in Leiden from July 20th to 25th 911.

The ionisation current in the main ionisation chamber was 100, expressed in arbitrary units (about 10 electrostatic units). he strength of the compensation current was so regulated that was a little larger. The difference was at most 20 units, bout 2 °/₀ therefore. The rays used for the experiments were amma rays.

We were able to make two experiments with liquid hydrogen. n the experiments the cold ionisation chamber, as we said bove, was filled with dry gaseous hydrogen, and by this we ade sure that no deposit could come on to the radium tube.

In the first experiment the current of originally 10.9 units, ttained the value of 14.7 units after the pouring in of the liquid ydrogen, which took 15 minutes. This change corresponds to a change in the main current of $0.34\ ^{\circ}/_{\circ}$. In the second experiment the current measured had a strength of 18.3 units, and was very constant, the irregularities measured during an hour were less than 1/10000 of the main current. After the liquid hydrogen had been poured into the apparatus, measurements which agreed very well with each other gave for the value of the current during half an hour 18.5 units, and after an hour 18.2 units. We can thus assert that in this experiment, which was evidently conducted under very favourable circumstances the cooling had not caused a change in the main current of as much as 1 in 5000.

We made another experiment at the temperature of liquid oxygen. The current measured had a strength of 1.8 units. Measurements made during an hour at the temperature of liquid oxygen gave a value of 2.6 units for the current measured, which corresponds to a decrease of 0.7 in 1000 in the main current.

It would have been desirable to have made a greater number of experiments and to continue these during a greater length of time; nevertheless it would appear to be justifiable even now to state, that *cooling of radium down to the temperature of liquid hydrogen (about* 20°.3 *absolute) during a period of not more than* $1^{1}/_{2}$ *hours does not cause a change in the gamma radiation of* 1 *in* 1000 *and probably not even of* 1 *in* 5000.

It is thus probable paying due regard to the degree of accuracy attained, that this decrease of temperature has no immediate or quickly decernable influence upon the emanation or the active deposits of short period (radium A, B and C). But in these experiments there was no opportunity for detecting an ultimate effect upon the radium itself, or a slowly developing effect upon its evolution products.

Experiments with polonium.

A few preliminary experiments on the influence of low temperatures upon the radiation of polonium have been made in Paris. The experiment which was made only with liquid air gives rise to some difficulties. A plate on which was some deposit of polonium was placed at the bottom of a long glass tube, which

p. 14 line 9 „ „ „ for ultimate read eventual.

could be immersed in liquid air. This plate radiated through a thin aluminium plate that closed the tube, into an airtight ionisation chamber, where the polonium rays were absorbed by the air. The polonium tube was as far as possible exhausted; and the vacuum was further improved by immersing a side tube containing a little charcoal in liquid air. The radiation was measured at ordinary temperature, and later, when the bottom of the tube was immersed in liquid air. In these experiments changes of current of inconstant amount were observed when cooling was applied. These changes were smaller in proportion as the vacuum was made more complete and kept more constant. It is thus highly probable that they were entirely due to the nfluence upon the polonium of the condensation of gases still present in the apparatus.

Experiments made in Leiden in liquid hydrogen with a provisional apparatus have convinced us that one might get rid of the condensations completely, even with liquid hydrogen, by using a ionisation chamber filled with pure gaseous hydrogen and a side tube with charcoal, immersed in liquid hydrogen.

Conclusions.

All these experiments which unfortunately are not so complete as we could have wished, confirm the independence of the radiation from the temperature, over a larger range of temperatures than had heretofore been done. Moreover these experiments have brought to light sources of error which must be taken into account, if one wants to make very accurate measurements at low emperatures.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 136.

J. P. KUENEN and S. W. VISSER. A Viscosimeter for volatile liquids.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akademie van Wetenschappen te Amsterdam*, **31 Mei 1913**, p. 22—32).

EDUARD IJDO — PRINTER — LEIDEN.

J. P. KUENEN and S. W. VISSER. *A Viscosimeter for volatile liquids.*

In determining the viscosity of a volatile liquid it is necessary to take the measurements in a closed viscosimeter. It is moreover desirable that the apparatus should be small, so that it can be easily handled and the temperature can be easily kept constant in all parts, and that the liquid does not come in contact with mercury; the use of mercury at temperatures below its freezing-point is in any case excluded.

In designing an apparatus that should fulfil these requirements, we based ourselves upon OSTWALD's viscosimeter ¹) His viscosimeter consists of a glass U-tube with one wide and one capillary arm; the wide tube has a bulb at the bottom, and the capillary tube one at the top. The capillary tube opens at the bottom into a wider tube, which curves into the lower bulb. The time which the liquid takes to pass from the bulb through the capillary tube into the bottombulb is observed. The experiment begins when the liquid surface passes a contraction above the bulb, and ends when it reaches the capillary tube. Before each determination the liquid is drawn up through the capillary, or pressed up from the other side.

The first thing that we tried to do was to make this viscosimeter into a closed apparatus by joining the two branches of the U-tube above into an 0; our intention was to collect the liquid every time in the upper bulb by simply turning the apparatus upside down.

This was not successful, as the liquid would not join in this position, some of it remaining in the wide tube above the capillary.

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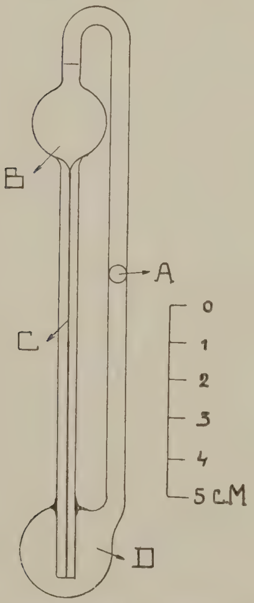
¹) OSTWALD, Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen. 1893, p. 195.

On this account the bottomreservoir was blown directly onto the capillary tube, and the wide tube was then sealed to it in the immediate vicinity of the capillary tube. By this means the apparatus became more compact, as the curved portion of the wide tube disappeared.

Still liquid remained above the capillary tube, which prevented it readily flowing back. Moreover the time which the liquid took to pass through appeared to depend upon the way in which the liquid flowed out of the capillary tube along the walls of the bulb.

Finally, the capillary tube was provided with a continuation reaching nearly to the bottom of the bulb. When the apparatus is turned upside down the extremity of the capillary tube projects above the liquid; and the liquid runs back without any difficulty. During the determination the liquid now flows out continually under the liquid surface. As the figure shows in making this apparatus a hole is blown in the bulb; through this the capillary tube is introduced and the two are then sealed together. The final form of the apparatus is sufficiently clear from the figure. The liquid is introduced by the side tube *A*; after filling this is sealed off. In the inverted position the liquid fills the bulb *B*, and part of the wide tube. If the viscosimeter is then turned up again, the liquid flows partly out of the wide tube to the bulb in which the capillary tube ends, the flow through the capillary tube begins at the same time, the meniscus passes along the upper curve; at the moment that liquid passes a mark above the bulb *B*, a chronometer is set going. This mark takes the place of the contraction in Ostwald's viscosimeter, where a drop of liquid is apt to collect. Through the capillary tube *B* is now emptied. The chronometer is stopped when the liquid dips into the capillary. The apparatus can then be turned upside down again, and the bulb quickly empties itself again.



The viscosimeter is placed in a wider tube, in which a bath of constant temperature is maintained; this tube is put up in such a way, that it can easily be turned upside down.

The whole apparatus is not more than 15 cm. long, and by taking a finer capillary tube, or a larger bulb, it can be made even a little shorter.

No absolute determinations were made. The times of flow for various liquids were compared to that of water.

Some preliminary measurements were made with a larger experimental tube. In the final apparatus the dimensions used were such that in determining the viscosity of normal butane, a period of flow of at least three minutes could be reckoned upon. In the preliminary determinations a difficulty showed itself; in turning the apparatus over, the small bulb did not easily fill itself, on account of the great capillarity of water. With liquids such as aether and alcohol no difficulty was experienced. It seemed probable that determinations with water would be impossible with a much narrower tube The apparatus was therefore standardised with water, before the *U*-tube was closed, while the apparatus was still used like Ostwald's viscosimeter.

Influence of the quantity of liquid.

The time of flow depends upon the total amount of liquid in the apparatus. The more liquid there is, the higher the surface is in the lower bulb, and the smaller is the pressure under which the liquid flows.

In Ostwald's viscosimeter the same volume is taken of the various liquids: in this way the influence of the filling of the viscosimeter is eliminated When the apparatus is filled with a liquid of high vapourpressure, or liquid gas, it is difficult to fulfil accurately the condition of equal volumes, and it becomes necessary to investigate experimentally the influence of the volume of liquid. This can be done by measuring the time of flow of the same liquid, e. g. water, with various fillings. If we then know the weight of another liquid used, and its specific gravity, we know the total volume. From the measurements previously made with water we can then find the time of flow for the same amount of water. From the ratio of the times of flow (t and t_w) the viscosity (η) is then calculated by the equation

$$\eta : \eta_w = d\,t : d_w\,t_w.$$

Influence of capillarity on the time of flow.

In consequence of the capillary action the pressure is not that of the mean difference of height, but is smaller. It is sufficient to make an estimation of this correction.

The capillary rise in a tube which is placed in side a second tube is given by the formula

$$h = \frac{2\sigma}{dg}\left(\frac{1}{r} - \frac{1}{R - r_1}\right),$$

in which σ represents the capillary constant, d the density, r the internal radius of the first tube, R the internal radius of the second tube. By this formula the capillary rise was calculated for a series of positions of the liquid surface during the flow; further the volumes between the chosen positions were estimated and by means of these the times elapsing between the moments at which the positions were reached. The capillary ascension was then represented graphically as a function of the time and by means of the curve the mean rise was determined. This devided by the mean height of the liquid gives the correction for the capillarity in percentages.

For water at 0° with $\sigma = 75.5$ we found: mean capillary rise 0.034 cM.; the mean height of pressure is 11.6 cM., which gives for the correction 0.3 %. For water at 30° with σ 71.0 it is also 0.3 %.

The capillary rise of water in the capillary at 0° was 8.0 cM., that of butane at the same temperature 2.4 cM.; the correction for the time of flow was therefore for butane 0.09 %: this may be regarded as constant in the field of temperature used.

Reynolds' *critical velocity.*

To make sure that the velocity of the liquid remained below Reynolds' critical value, an estimation was made. The volume of the upper bulb was about 3.5 ccM.; the capillary tube was fully 11 cM. long, the diameter of the capillary tube D was

0.038 cM, the viscosity η is about 0.002, the density d at 0° is 0.60, and the time of flow 300 seconds. With these data we find for $\frac{Ddv}{\eta}$ the value 117, which is far below Reynolds' critical value (2000).

Determinations with water. Influence of the temperature.

The water used was doubly distilled. Great care was taken to keep it free from dust. It was renewed from time to time, which had however very little influence upon the results.

The viscosimeter was placed in a waterbath, which was kept in circulation by a rotating screw, and at constant temperature by means of an adjustable number of platinum spirals through which an electric current was passed. Everything was bound round with cottonwool, which was partially removed at the beginning and end of the timedeterminations. The temperature was read every minute. The greatest difference during one observation was 0.07°, in the second series during 54 minutes it was 0.

During the measurements at 0° the viscosimeter stood in ice.

The two ends of the U-tube were covered by glass caps. After each determination the liquid was sucked up by a water pump.

I	temp.	time.	II	temp.	time.
31 Oct. '12	26.05	12 m. 11.4 s.	1 Nov.	26.48	12 m. 6.8 s.
	25.99	11.4		26.48	6.7
	26.03	11.6		26.48	6.2
	26.03	11.7		26.48	6.6
	26.05	11.2			
mean	26.03	731.5 s.		26.48	726.6 s.
Corrected for capillarity		729.3 sec.			724.4 sec.

III	temp.	time.	IV	temp.	time.
5 Nov.	0.00	24 min. 59.7 s.	7 Jan. '13	0.00	24 min. 57.2 s.
		59.7			57.2
		59.6			56.9
					57.0
					56.7
mean	0.00	1499.7 s.		0.00	1497.0 s.

Mean time of flow at 0° 1498.5 sec.

Corrected for capillarity 1494.0 sec.

Specific gravity of water at 0° 0.9999; at 26.48° 0.9967; at 26.03° 0.9968.

$$\eta_0 : \eta_{26.48} = 1493.9 \times 0.9999 : 724\ 4 \times 0.9967 = 2.069$$

$$\eta_0 : \eta_{26.03} = 1494.0 \times 0.9999 : 729.3 \times 0.9968 = 2.055$$

Thorpe and Rodger [1]) give for the viscosity of water at

0°	0.01778
25°	0.00891
30°	0.007975

Bingham [2]) assumes the reciprocal of η as a linear function of the temperature. From Thorpe a Rodger's figures follow:

at 0° $\frac{1}{\eta}$	= 56.2
„ 25°	112.0
„ 30°	125.4

From this follows:

by 26.48° $\frac{1}{\eta} = 115.97$ by 26.03 114.76

For the ratio of the viscosities at 26.48° and 0° we find from this:

$$\frac{\eta_0}{\eta_{26{\cdot}48}} = \frac{115.96}{56.2} = 2.063$$

and

$$\frac{\eta_0}{\eta_{26{\cdot}03}} = \frac{114.76}{56.2} = 2.042$$

Our result at 26.48, 2.069, agrees with this to less than $^1/_3$ %, which may be regarded as sufficient. The agreement of the other figures is a little less satisfactory (about 0.7 %), which is probably the consequence of the less perfect equilibrium of temperature.

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[1]) Thorpe and Rodger. On the relations between the viscosity of liquids and their chemical nature (Phil. Trans. 185 A, p. 449, 1894).

[2]) Eugene C. Bingham and Miss J. Peachy Harrison, Viskosität und Fluidität Z.S. f. Physik. Ch. 66, p. 1, 1909.

Eugene C. Bingham, Viscosity and Fluidity, a Summary of Results Phys. Rev. XXXV, p. 407, 1912; Phys. Rev. (2) I, p. 96, 1913.

Influence of the total quantity of water.

All the determinations were made at 0°.

Small quantities of water were added or drawn off. After each series of determinations the viscosimeter was weighed with water, and at the end the empty viscosimeter. From this follows the volume of water at each determination. Usually two measurements were made in each series. The greatest difference between them was 1.4 sec. in a total time of 25 minutes, a difference of less than 0.1 %.

The results were the following:

	weight of water.	time of flow.
10 Jan. 1913	3,24 gram.	1470,3 sec.
10 „ 1913	3,53 „	1480,2 „
7 and 8 Jan.	4,06 „	1497,0 „
8 „	4,41 „	1516,3 „
11 „	4,42 „	1517,2 „
9 „	4,88 „	1528,3 „
9 „	5,24 „	1544,4 „

Graphically represented these figures give a curve with two points of inflexion. If the bottomreservoir were cylindrical, the curve would be a hyperbola, as the product of pressure and time of flow is constant. The deviation from the hyperbola which the curve shows, can be explained in every particular by the irregular form of the bottom reservoir (bulb with a tube sealed in at the side).

Determinations with Normal Butane

The sidetube A was connected to the reservoir which contained the butane prepared according to GRIGNARD's method [1]). After the viscosimeter had been pumped out, the butane was distilled over. For this purpose the lower bulb was cooled in a mixture of ice and. salt. After cooling the sidetube was sealed off.

The determinations above 0° were made in a waterbath, like the determinations with water. The glass jacket, which consisted of two coaxial tubes fastened by an india-rubber ring, was turned round with the viscosimeter. The latter was clamped between two corks in which a number of holes were bored. No determinations were made above 35°, as then the internal pressure may exercise a very uncertain influence upon the volume. The vapourpressure of butane at 35° is 3.6 atmospheres.

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[1]) J. P. KUENEN. Comm. N⁰. 125, p. 4, 1911.

At 0° the viscosimeter was placed in a wide testtube which was closed by a cork. Two glass tubes fastened with sealing wax into a strip of cork, made two openings in the ice for the observation of the beginning and end-points. The testtube stood vertically in ice, in which also two tubes left room for the observations. After one determination the testtube was lifted out of the ice, turned upside down, and put back in its place again after the upper bulb was filled.

Finally a determination was made in a bath of boiling methylchloride.

At the suggestion of Prof. Kamerlingh Onnes a vessel of german silver was constructed for this, in which the viscosimeter was suspended in methylchloride in such a manner that it could be turned round while inside and that the position of the liquid in the upper bulb could be observed. In the construction connections with substances like sealing wax which come into contact with the cold liquids have to be avoided. By this means we avoid contamination of the liquid, and cracking or giving way of the connections which the cold might cause. All connections are therefore made in the lid of the vessel. The three projections are represented in fig. 1, 2 and 3 at $^1/_5$ of the actual size. The details in fig. 4—6 are actual size. The vessel consists of a neck *H* of circular section, a wide part, of elleptical section, *E*, and the bottom, which consists of a semicircularly bent strip *R*, the diameter of which is equal to the large axis of the ellips and two curved sideplates P_1 and P_2 which complete the vessel. The vessel is provided with a number of strengthening rings *v* (necessary for working at low internal pressure) and stands in a box filled with cotton wool.

The viscosimeter hangs in the lower part of the vessel in a frame, *BG*, which is attached to a german silver tube *TS*, which

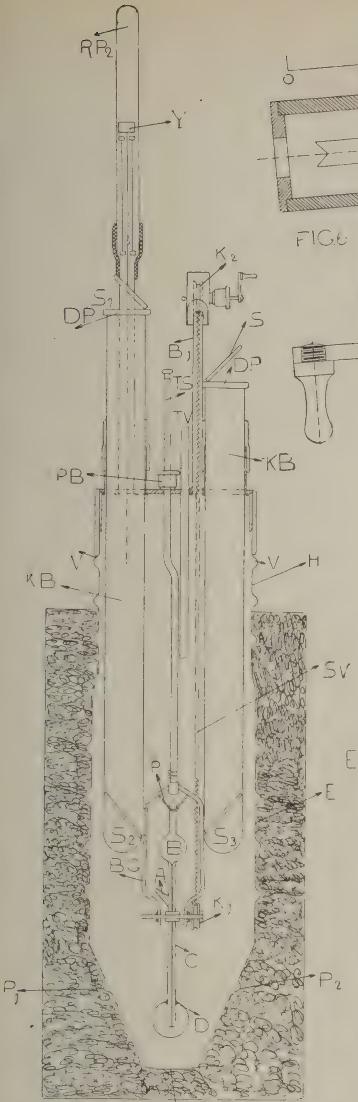


FIG.1

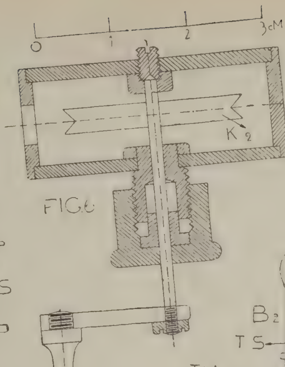
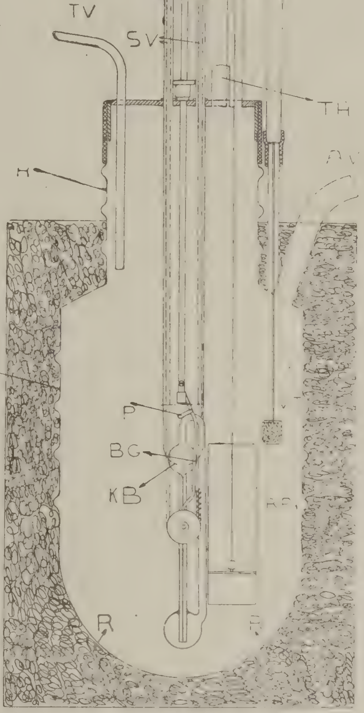


FIG.6



F.G.2

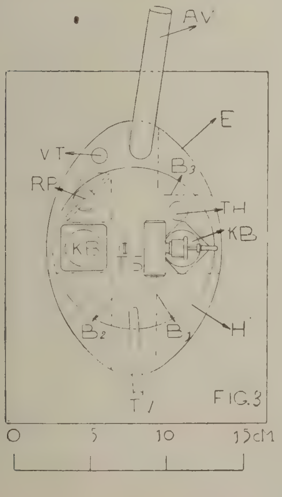


FIG.3

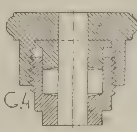


FIG.4

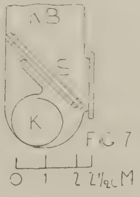


FIG 7

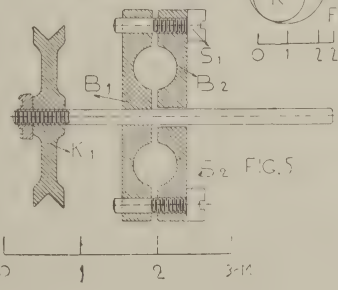


FIG.5

projects above the vessel through an opening. This opening is made air-tight by a stuffing box *PB* (fig. 4). The tube has a bend by which the opening in the lid comes just outside the middle, which is necessary in view of the available space. This tube can be moved up and down in the stuffing box.

The viscosimeter can be turned round an axle. (fig. 5) The two tubes of the viscosimeter wound round with silk are clamped between two blocks B_1 and B_2 by two screws S_1 and S_2. B_1 is soldered to the axle. The axle is provided with a pulley K_1, which is worked by means of an endless spiralspring *SV* (fig 1 and 2) by a second pulley K_2 in an airtight box above the lid of the vessel; the axle projects ontside through a stuffing box (see fig. 6). This pulley is raised up out of the way of the other parts on two tubes B_1 and B_2 soldered onto the cover, and through which the spiralspring runs. The frame *BG* is provided with a pall bound with silk, which prevents the viscosimeter going beyond the vertical position. The turning takes place in a plane parallel to the long axis of the ellips.

For the observation of the viscosimeter there are two view-tubes *KB* fastened into the cover in the direction of the short axis of the ellips, which reach below the upper bulb, (fig. 1 and 3). (In fig. 2, part of one of the tubes is shown). These tubes are closed air-tight above the cover by thick glass covering plates *DP*. The light of a glowlamp is thrown upon the viscosimeter by the mirrors S_1 and S_2, it can be viewed by the mirrors S_3 and S (fig. 1). The mirrors S_2 and S_3 (fig. 7) are attached to a copper cross which is soldered onto a hoop of copper wire *K*, resting upon the bottom of the view-tube, and by which the mirrors can be easily adjusted. When they are in the right position the wire is fastened with paraffine. Opposite to the mirror the view-tubes have a sideopening ground flat, onto which a covering glass is fastened with fishglue. This connection remains firm even in liquid air. By this means the light falls through a planparallel layer of liquid, so that the bulb does not appear distorted. To avoid the glue being exposed to pressure, there are openings higher up in the view-tubes (fig. 1). By moving the viscosimeter a short distance up and down with the handle *TS* the mark above the bulb or the beginning of the capillary tube can be brought into view. The spiralspring remains tight the whole time.

In addition the vessel contains:

1^0. an electro-magnetic stirringpump *RP* (fig. 2 and fig. 3; in fig. 1 a part of it). The iron core *IJ* is moved up and down by an electro-magnet round the tube RP_2. The bottom of the cylinder RP_1 and the piston are provided with suitable valves, turning on an axis represented in fig. 3 by a double dotted line. The shape of the cylinder is here shown also.

2^0. a floater which indicates the height of the boiling liquid.

3^0. a platinum resistancethermometer, of which only the tube sealed into the cover is shown: *TH* (fig. 2 and 3).

4^0. a supplytube for the liquid *TV*, which is closed after filling.

5^0. a tube *AV* to lead off the vapour, when working at low pressure.

6^0. three tubes B_1, B_2 and B_3 (fig. 3) which fill up the superfluous space, to save liquid and trouble.

When tested this cryostat appeared to be in every way satisfactory, the distinctness of the readings left nothing to be desired. At the same time the volume of the butane was so much diminished by contraction that it was difficult to get sufficient pressure when the viscosimeter was turned round, to drive the remaining liquid out of the capillary. Only one determination was successful. We hope later on to be able to publish more extensive determinations at low temperatures.

Our results are given in the table.

The liquid-densities were measured by a dilatometer.

temp.	time.	corrected.	density.	η
34.5°	235.5	235,2	0.556	0.00153
18.5°	258.5	258.2	0.577	176
0.0	291.8	291.5	0.601	207
— 23.6	352.6	352.3	0.631	265

The method of calculation of η from the data is made clear by the following example.

The viscosimeter when filled weighed 16.78 gr. empty 14.26 gr.

The weight of the butane was therefore 2.52 gram with a volume of 4.20 ccM.

The time of flow of 4.20 ccM. water at 0° is 1504.3 sec. (according to table on page 9) of the butane 291.8 sec.

Corrected for capillarity these times become 1499.8 and 291.5.

$$\eta_w = 0.01778\ ^{1)} \text{ therefore } \eta_b = 0.01778 \frac{0.601 \times 291.5}{1498.9 \times 0.9999} = 0.00207.$$

Thorpe and Rodger (p. 590) give for the viscosity at the bolingpoint for

normal	pentane	$\eta \times 10^5$	200	isopentane	203
„	hexane		204	isohexane	205
„	heptane		199	isoheptane	198
„	octane		198		

As the boilingpoint of butane is just below 0° the value we find for η corresponds well with that for the other hydrocarbons.

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1) Thorpe and Rodger l. c. p. 449.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 137^a.

◆

H. KAMERLINGH ONNES and C. A. CROMMELIN. Isothermals of di-atomic substances and their binary mixtures. XIII. Liquid-densities of hydrogen between the boiling point and the triple point; contraction of hydrogen on freezing.

(*Translated from: Verslág van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **28 Juni 1913**, p. 214—216).

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H. KAMERLINGH ONNES and C. A. CROMMELIN. *Isothermals of di-atomic substances and their binary mixtures.* XIII. *Liquid-densities of hydrogen between the boiling point and the triple point; contraction of hydrogen on freezing.*

Densities of liquid hydrogen have so far only been determined by DEWAR [1]. As a more accurate knowledge of this quantity is of importance for the equation of state the following measurements were undertaken. They were made with the same apparatus as served for argon [2].

The temperature was determined by measuring the vapour pressure of the hydrogen in the cryostat. The sensibility of this method is very great, as 1 mm. difference in vapour pressure corresponds to 0°.004 at the boiling point and to 0°.02 at the triple point. The measurement does not therefore require great care being taken. As shown by measurements by KAMERLINGH ONNES and KEESOM, the vapour pressure may be determined by reading the pressure in the cryostat itself, instead of in a special vapour pressure tube filled with pure hydrogen and placed in the cryostat, if an accuracy of 0°.02 or 0°.03 is considered sufficient.

The temperature on the KELVIN-scale [3] corresponding to these vapour pressures are taken from measurements by KAMERLINGH ONNES and KEESOM, not yet published [4]. Their results have not been definitely calculated, but the small corrections which may be as yet required are of no importance for the object of this paper.

For the method of calculating the volumes we may refer to the paper on the diameter of argon quoted above.

The results are contained in the table. It also gives the densities calculated by the quadratic formula

$$\rho_{T\,\mathrm{liq}} = a + bT + cT^2$$

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[1] J. DEWAR, Proc. R. S. (A) 73 (1904) p. 251

[2] E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN, Comm. N°. 131*a*.

[3] The corrections for the reduction of the hydrogen-scale to the KELVIN-scale are given by H. KAMERLINGH ONNES and W. J. DE HAAS, Comm. No. 127*c*.

[4] Cf. Comm. N°. 137*d*.

with the following values of the constants:

$$a = + 0.084404$$
$$b = - 0.0002230$$
$$c = - 0.00002183$$

made to fit the readings at — 258°.27, — 255°.99 and the boiling point.

The deviations from this formula will be seen to be very small; they are within the limits of accuracy of the observations, except possibly at the highest temperature. It may be added, that the density at the boiling point was not directly observed, but was calculated from the neighbouring observations.

The first column contains the number of the observation, the second the temperature below 0° C., on the KELVIN-scale, the third the density observed referred to the density of water at 4° C., the fourth the density according to the formula and the fifth the difference of the latter two.

N⁰.	θ	$\rho_{\Gamma\ liq}$ *obs.*	$\rho_{\Gamma\ liq}$ *calc.*	*obs.—calc.*
VIII	— 252.68	0.07081	0.07076	+ 0.00005
—	— 252.77 boiling point	7086	7086	—
XIV	— 253.24	7137	7138	— 1
XIII	— 253.76	7192	7194	— 2
XII	— 255.19	7344	7342	+ 2
XI	— 255.99	7421	7421	—
X	— 256.75	7494	7493	+ 1
III	— 257.23	7538	7538	0
IX	— 258.27	7631	7631	—

In addition to the liquid-densities the density of solid hydrogen was also determined. It was first of all ascertained that *solid hydrogen is heavier than liquid hydrogen* and, therefore, that *on freezing contraction takes place.* For this purpose the hydrogen in the cryostat was frozen; a solid crust is then formed on the liquid. If the pressure is now made to rise slowly, this crust divides into fragments which sink down in the liquid and collect at the bottom of the vacuumglass. It was not till this observation was made, that we ventured to freeze the hydrogen in the dilatometer without fear of bursting the very carefully calibrated instrument.

In order to be sure, that the freezing would proceed from the bottom, the tube of the dilatometer was movable in a stuffing box, which was fitted in the lid of the cryostat. After the hydrogen in the cryostat had been frozen to an opaque solid mass, the dilatometer was pushed down slowly. The hydrogen in the dilatometer was then frozen to a homogeneous transparent mass. At the moment of reading the volume of the solid hydrogen, the pressure in the cryostat was 0.66 cm.

In order to obtain an estimate of the temperature, the vapour pressures of solid hydrogen being practically unknown, the vapour pressures according to KAMERLINGH ONNES and KEESOM were extrapolated by means of the log p, $\frac{1}{T}$-diagram, in which the vapour pressure curves are known often to be very nearly straight lines, neglecting the break in the curve at the triple point. In that manner the temperature θ corresponding to a pressure of 0.66 cm. was found to be

$$-262^\circ.0.$$

The density of solid hydrogen at this temperature was found to be

$$\rho_{\Gamma\text{sol}} = \underline{0.08077.}$$

Putting the triple point temperature, according to the same measurements at

$$\theta_{\text{coex. liq. vap. sol}} = -259^\circ.2$$

extrapolation by means of the above formula gives for the liquid density at that point

$$\rho_{\Gamma\text{coex. liq.vap.sol.}} = \underline{0.07709.}$$

Assuming that the density of solid hydrogen at the triple point does not differ appreciably from that at -262°, the contraction on freezing is found to be about 4.8 $^0/_0$ of the liquid-volume.

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H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 137^b.

H. KAMERLINGH ONNES and SOPHUS WEBER.

Vapour pressures of substances of low critical temperature at low reduced temperatures. I. Vapour pressures of carbon dioxide between −160° C. and −183° C.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **28 Juni 1913**, p. 226—239).

EDUARD IJDO. — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and SOPHUS WEBER. *Vapour pressures of substances of low critical temperature at low reduced temperatures* I. *Vapour pressures of carbon dioxide between* —160° C. *and* —183° C.

§ 1. *Introduction.* The knowledge of the vapour pressures of substances of low critical temperature at low reduced temperatures has recently obtained special importance [1]. The gradual transformation shown by the reduced equations of state for various substances, when ordered according to their critical temperature, manifests itself in particular in the gradual transformation of the reduced vapour pressure curves and the deviations from the law of corresponding states, which show themselves clearly in this transformation and are connected with NERNST's heat-theorem, have acquired increased importance by the connection with PLANCK's theory of energy-quanta.

We have therefore undertaken a series of determinations of vapour pressures for substances of low critical temperature at lower temperatures than in previous determinations. The measurement of the very low vapour pressures with which we are concerned in this case forms a separate branch of research. In measuring the pressure in a space at ordinary temperature, connected by a tube with the space, where the vapour and liquid or solid are in equilibrium at a known low temperature, correct results can only be arrived at, if due regard is paid to the theory of the thermal molecular pressure.

KNUDSEN [2], who has developed this theory, has shown that, when a temperature gradient exists along a closed tube containing a gas in equilibrium, there will in general be a pressure difference between the ends of the tube, such that the higher pressure is observed where the temperature is higher The magnitude of the difference depends on various circumstances, specially on the ratio of the radius of the tube R to the free path of the gas molecules λ. In the limiting cases, calling p_1 and p_2 the pressures, T_1 and T_2 the absolute temperatures at the ends, we have

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[1] For the literature and a discussion of the questions referred here, see: H. KAMERLINGH ONNES and W. H. KEESOM: Die Zustandsgleichung. Enc. d. math. Wissensch. V. 10. Leiden Comm Suppl. N°. 23.

[2] MARTIN KNUDSEN: Ann. d. Phys. Bd. 31 p. 205, 1910.
" " " " 31 " 633 "
" " " " 33 " 1435 "

1°. $$\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}} \text{ for } \frac{R}{\lambda} = \frac{1}{\infty}$$

2°. $$p_1 = p_2 \text{ for } \frac{R}{\lambda} = \infty .$$

For intermediate cases KNUDSEN deduces more complicated formulae which may be applied over a wide range. As a rule the matter reduces itself to the application of a correction to one of the limiting cases. The application of the formulae is not allowed over the range defined by

$$1 < \frac{2R}{\lambda} < 10.$$

When these limits are exceeded, the accuracy very soon falls below 1 °/₀. It is necessary, therefore, to avoid the above range in the measurements by a suitable choice of the tubes connecting the evaporating surface with the measuring apparatus, and by changing them, when occasion arises. When this is found to be impossible, the measuring apparatus will have to be kept at a temperature but little higher than that of the liquid or the thermal molecular pressure will have to be measured experimentally or a different method altogether will have to be resorted to ¹).

In the range where the measurements can be corrected to the limiting cases by means of the more complicated formulae referred to it may occur, that the corrections cannot be applied for a given tube owing to the free path being unknown and that this quantity cannot be found with sufficient accuracy by extrapolation: in that case the object can be attained by means of measurements with two different tubes suitably chosen, so as to eliminate the pressure and to obtain data for the calculation of the free path, which can then be introduced into the formulae.

The pressures which we wished to measure lie between 0.002

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¹) E. g. KNUDSEN's method of molecular effusion through a small orifice, in which the amount of vapour passing through is measured instead of the pressure.

baryes and 1 mm. The highest of these might still have been measured with a MAC LEOD gauge, but for the lower ones this method is not applicable owing to the possibility of mercury distilling over at the low pressure to the cold substance. We have therefore used KNUDSEN's heated wire gauge [1]) between 1 mm. and 0.001 mm. and KNUDSEN's absolute manometer [2]) between 0.002 baryes and 0.001 mm.

§ 2. *The absolute manometer.* From the different forms described by KNUDSEN we chose one without sealed on windows or ground joints in order that the apparatus could be heated to 300°. This heating is advisable for the purpose of removing the occluded gases from the metallic parts and so obtaining a permanent high vacuum. The working part of the manometer is represented in fig. 1. A german-silver tube *B* of 1 mm. wall thickness was flattened by means of a roller and provided with a loose lid *D*, while the lower end remained open. V_1 and V_2 are the two windows through which the molecules enter the tube: they proceed from the wall of the glass vessel in which the tube is contained and which is alternately at a high and at the ordinary temperature and strike against the mica-plate *M*, movable round a vertical axis, on which they exert a turning moment which at a given temperature is proportional to the pressure. The plate *M* is suspended from a platinum strip (obtained by rolling out a platinum wire of 0.08 mm.) and is provided with a piece of iron (length 2 mm., diameter 0.07 mm.) for the purpose of regulating the sensibility by means of a magnet. The platinum strip is hard-soldered

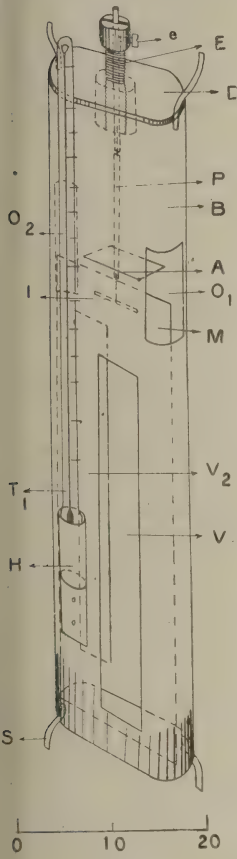

Fig. 1.

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[1]) MARTIN KNUDSEN, Ann. d. Phys. Bd. 35, p. 389, 1911.

[2]) MARTIN KNUDSEN, Ann. d. Phys. Bd. 32, p. 809, 1910.

to thicker platinum wire at both ends. The lower wire is connected to *M*, the upper one passes through the screw *E* and is clamped with the screw *e*. By means of *E M* can be made exactly parallel to the flat sides of *B*.

A is a platinum wire which prevents the mica plate falling down when the apparatus is inverted.

The two windows O_1 and O_2 serve for the reading of the rotation of *M*: for this purpose the outer edge of the mica plate is observed in a LEITZ reading microscope with eye-micrometer. The temperature of the german-silver tube is read on a thermometer which is in metallic connection with it and protected from radiation by means of the tube *H*.

The tube *B* is held in the glass vessel (fig. 2) by the springs *S*.

The dimensions of the various parts of the apparatus were as follows:

area of V_1	9.030 . 1.18 cm².
„ „ V_2	9.005 . 1.20 cm².
distance between the centres of V_1 and V_2 (arm of couple)	1.190 cm.
length of mica plate	12.70 cm.
width „ „ „	3.117 cm.
moment of inertia	1.415 gr. cm².
time of swing (full period)	3.53 sec.

magnification of microscope: 4 mm. = 87.5 scale divisions on micrometer.

In fig. 2 is shown the manner in which the manometer was mounted.

The tube *B* is placed inside a glass tube which is provided with a water-mantle *W*; through *W* hot or cold water can be passed as required, by means of the pinching screws K_1 and K_2. The temperature of the mantle is read on the thermometer T_2.

The vapour pressure tube *R* which is sealed to the manometer tube, bent over and closed at the bottom, is placed in cryostat with a calibrated resistance thermometer which gives the temperature of the evaporating surface. The diameter of the tube *R* was 1.71 cm.

The best method of securing an even temperature in the cryostat is stirring with a "pump-stirrer", in this case however, as the smallest vibrations disturb the readings of the manometer, preference was given to the use of a stream of vapour-bubbles evolved by local heating with an electrically heated wire.

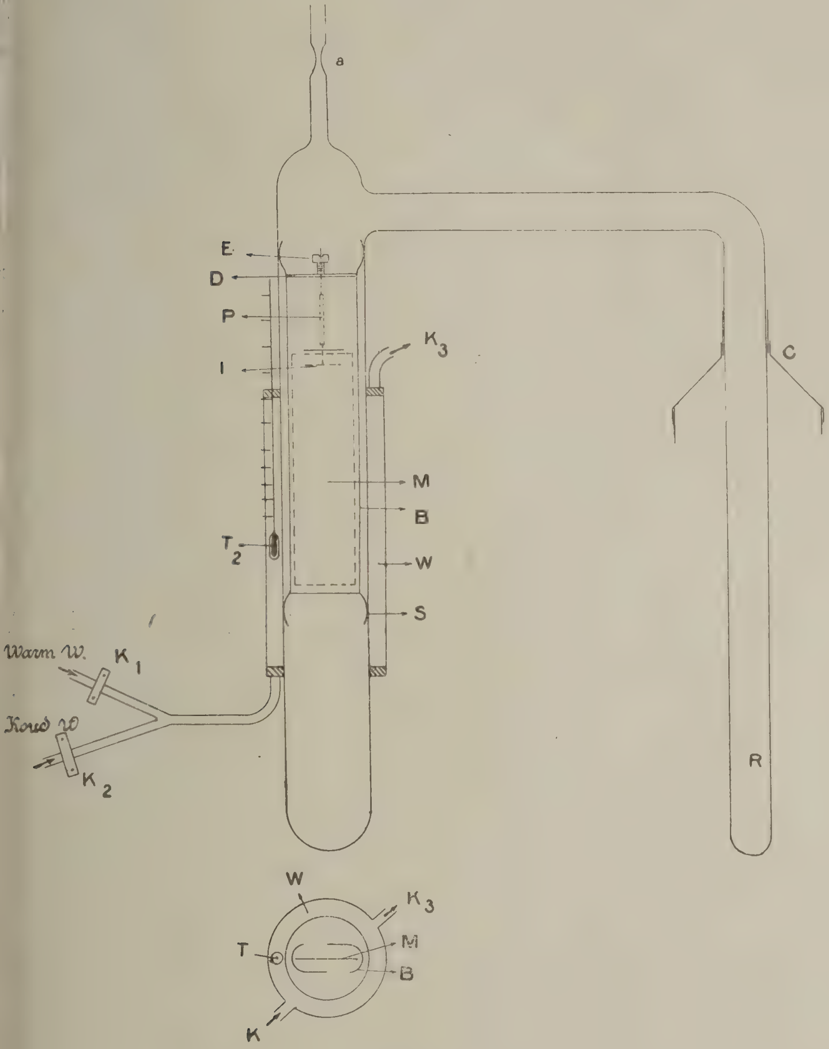

Fig. 2.

§ 3. *Calibration of the absolute manometer.* In the first place it was necessary to consider for what range of pressures the manometer may be used as an absolute instrument. In the second place seeing that the distance of the mica plate to the windows V cannot be treated as infinitely small and the sensibility can thus only be calculated approximately, the value of a scale reading at given difference of temperature between outer wall and mica plate must be expressed in baryes.

According to KNUDSEN the force per cm^2. K on the plate in the limiting case, when the mutual collisions of the molecules may be disregarded, is given by

$$K = \tfrac{1}{2} p \left(\sqrt{\frac{T_1}{T_2}} - 1 \right),$$

where p stands for the pressure, T_1 and T_2 for the temperatures of plate and wall respectively.

As regards the condition under which this formula may be used, it is found that in order to reach an accuracy of $^1/_2$ % in the final result, the free path must be at least ten times the diameter of the tube. The range of the manometer is thus different according to the gas used. For carbon dioxide according to BREITENBACH's measurements of the viscosity at 20° $p.\lambda = 7.4$, if p is expressed in baryes and λ is the mean free path in cms. From this it follows that the range of our gauge reaches up to about 0.3 barye.

The range can also be determined by connecting the manometer with spaces, where known pressures are established, and ascertaining for what pressures the elongation remains proportional to the pressure. In any case it is necessary, with a manometer such as ours which, as we have seen, does not allow the calculation of the reduction factor from the dimensions of the apparatus, to make measurements for the ditermination of this factor. By extending the calibration to pressures at which the elongation is no longer proportional to the pressure (supposing the rotation in any case to be infinitely small) the apparatus can be made into a pressure-indicator for that range, instead of an absolute manometer.

For the purpose of the calibration the manometer was connected with a system of pipettes according to KNUDSEN [1]), for the description of which we refer to a subsequent paper [1]. The results are contained in the following table:

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[1]) MARTIN KNUDSEN, l. c

TABLE I.

Calibration of the absolute manometer.

Approximate pressure in baryes.	Δ abs. man.	Δ according to pipettes in baryes.	$\frac{\Delta \text{ pip.}}{\Delta \text{ abs. m.}}$
0.147			
	0.427	0.390	
0.574			
	0.357	0.385	
0.931			
	0.303	0.381	
1.234			
	0.263	0.376	
1.497			
	0.214	0.372	
1.711			
0.056			
	0.114	0.1005	0.881
0.170			
	0.113	0.0996	0.881
0.283			
	0.110	0.0984	0.895
0.393			
	0.107	0.0972	0.908
0.500			
	0.105	0.0960	0.914
0.605			

The first colum gives the pressures calculated according to the indications of the absolute manometer by the formula

$$\frac{1}{2}\, p \left(\sqrt{\frac{T_2''}{T_1''}} - \sqrt{\frac{T_2'}{T_1'}}\right) = c\,(\alpha_1 - \alpha_2)$$

where T_2'' and T_1'' represent the temperatures of outer wall and mica plate (properly speaking tube B) respectively in the experiment at higher temperature, T_2' and T_1' the corresponding temperatures in the experiment at the ordinary temperature, c the value of the reduction factor calculated from the dimensions of the apparatus (as we have seen this calculation can only give an approximate value), α_1 and α_2 the two elongations. The second column gives the differences of the successive pressures, the third the same differences according to the observations with the pipettes.

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[1] S. WEBER. Vapour-pressures etc. II. The vapour-pressures of carbon dioxide between —140° C and —160° C. Comm. N^0. 137*c*. The same pipettes have also been used for the calibration of a hot-wire manometer for the purpose of thermometric measurements, which will be discussed in future communications about experiments with liquid helium.

In the first series the limits of proportionality are evidently far exceeded: it can therefore serve as a calibration of the manometer as a pressure-indicator. The second series shows clearly that at first the absolute manometer gives greater values for the pressures than the pipettes, which are however in a constant ratio to the latter, while later on its readings are lower than those of the pipettes, as might be expected [1]). It is also intelligible that our manometer gives higher readings in the beginning than the pipettes considering that the distance between the windows and the mica plate cannot be taken as small as compared with the width of the windows, so that parts of the movable mica plate outside the perpendicular projection of the windows will also be struck by molecules which proceed from the heated wall. This action along the edges owing to which c can only be approximately calculated was considerable in our case; its influence on the pressure follows immediately from the above calibration numbers: obviously c has to be replaced by

$$\frac{1}{0.881}\,c = 1.135\ c.$$

§ 4. *The measurements.* α. The manometer mounted as in fig. 2 was then exhausted for a long time under strong heating to 300° C.: for this purpose it was joined to a Gaede molecular airpump, for the loan of which we are indebted to the kindness of Leybolds Nachf. of Cologne, which we here gratefully acknowledge. As appears from the measurements communicated below it is possible to use this excellent, reliable and easily worked instrument continuously at pressures of 0.007 barye without the least trouble. After having been connected to the pump at the temperature mentioned for about a day the manometer ceased to give off gas. The vacuum had become constant. The small remaining pressure was thereupon measured, while the vapour pressure tube R was first placed in liquid oxygen and afterwards in methane of different temperatures. It appeared that the vacuum remained constant within the limits of accuracy and was independent of the temperature of the vapour pressure tube [1]). Carbon dioxide carefully dried and repeatedly distilled in vacuo was now introduced through a side tube into the tube R, which was cooled with liquid air. When a sufficient quantity had passed over, the apparatus was again connected to the molecular pump and evacuated during a considerable time. The manometer was then sealed off from the pump at a and the pressure measured, while R was surrounded with oxygen boiling under reduced pressure. It was found that the vacuum was the same as before the introduction of carbon dioxide, from which it follows that at —205° C. the vapour pressure of carbon dioxide must be smaller than 0.005 barye. A difference of 0.002 barye could be clearly detected and the influence of vibration was also just below this value; 0.005 barye could thus not escape observation.

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[1]) Debije (Physik. Z.S. 1911, p. 1115) has tried to represent this behaviour by a formula of approximation.

β. As a rule the further observations were made in the following manner: first the manometer is brought approximately to temperature-equilibrium, and the thermometers T_2 and T_1 are read; warm water is then made to pass through K_1 until a suitable temperature is reached; T_2 and T_1 are again read and the reading on the eye-micrometer is taken. Finally cold water is let into K_2, until T_1 has about assumed the original temperature, after which a second observation is made at the same temperature.

The calculation is made in the manner explained in section 2.

As described the vacuum was measured before carbon dioxide was admitted, R being at temperatures between —160° C. and

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[1]) The radiation-pressure did not amount in our case to more than $0.05 \cdot 10^{-3}$ barye, when the wall was at 100° C.

—200° C., when 0.007 baryes was found for the pressure. After sealing off the same value 0.007 baryes was found. A complete series of observations was then taken, first with methane and then with oxygen in the cryostat. The apparatus was then left standing for a few days, after which a new series of observation was taken. In the mean time the vacuum appeared to have risen to 0.016 baryes. If this change is taken into consideration the two series agree well with each other.

In table II the two sets of measurements are combined.

TABLE II.

Vapour pressures of carbon dioxide at temperatures between —183°.0 and —167°.04.

Temp. T —273°.09 K.	Pressure observed in baryes diminished by residual pressure.	Vapour pressure in baryes	Calculated according to NERNST.
—183°.0	0.015	0.008	0.0067
179.60	0.047	0.026	0.0241
175.37	0.179	0.106	0.1012
171.01	0.620	0.404	0.4083
168.83	1.143	0.791	0.7782
167.04	1.780	1.310	1.297

The figures in the 3rd column are derived from those in the 2nd by correcting for the thermal molecular pressure. This was done by means of the formula given by KNUDSEN:

$$\frac{p_1}{p_2} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{2} \cdot \frac{1}{1 + \frac{2R}{\lambda}}}$$

where p_1 and p_2 are the measured pressure and the real pressure respectively, T_1 and T_2 the corresponding temperatures, $2R$ the diameter of the vapour pressure tube and λ the mean free path calculated from $p\lambda = 4$. This relation was thus also applied in conditions, where the mean free path is not well represented by SUTHERLAND's formula [1]: this may, however, be considered allowable in view of the small influence of the term $\frac{2R}{\lambda}$.

It will be seen that the main term of the correction is large: but its value is accurately known and is in no way connected with the additional correction for λ. The latter is only of importance in the last measurements.

It is possible by a suitable choice of the radius of the vapour pressure tube R to make the additional correction so small, that it may be entirely neglected. It is our intention to do this in future experiments in order to become entirely independent of the small uncertainty arising out of this cause at present. In those experiments a little more time will have to be allowed for the setting in of the equilibrium pressure.

§ 5. *Determinations with the hot-wire manometer.* With regard to the choice of the shape and dimensions of the vapour-pressure tube R, used in the measurements with the absolute manometer, the question arises whether sufficient account has been taken of two causes of disturbance which may influence the results obtained. The tube being long cannot in itself be considered a sufficient precaution to exclude radiation from above, by which the temperature-equilibrium of the evaporating surface is rendered uncertain; furthermore it has to be ascertained, whether the surface of the liquid bath may possibly be at a lower temperature than the bath at the spot, where the temperature is measured [2].

In view of the degree of accuracy of the measurements with our absolute manometer the errors arising out of these causes of disturbance may be neglected.

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[1] The circumstance that in the exponential form the same factor is here used for the residual pressure, although the substance to which this pressure is due, is unknown, is of no importance within the limits of accuracy of the experiments.

[2] Comp. KAMERLINGH ONNES and BRAAK, Comm. N°. 107*a*. Even after 6 hours there was no sign whatsoever of a distillation of carbon dioxide at the bottom of R to the neighbourhood of the level of the liquid in the bath.

With our hot-wire manometer the accuracy which could be attained in the region of less low pressures, at which measurements were also intended, was considerably higher. In designing the vapour pressure apparatus intended for the measurements with this manometer the possible influence of the aforesaid causes of error was therefore carefully avoided.

The hot-wire manometer which we used is represented in fig. 3.

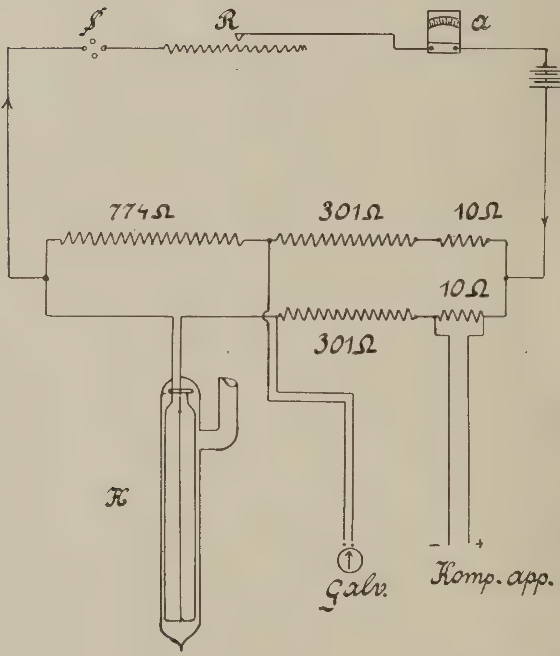

Fig. 3.

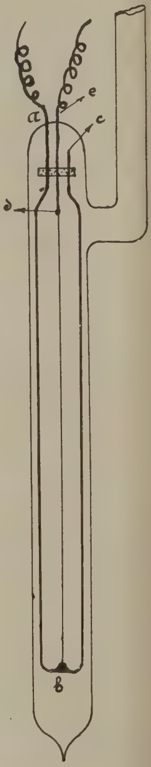

Fig. 4.

It consists of a Wollaston-wire (0.005 mm. in diameter and about 10 cm. long), stretched in a frame of platinum wire *abc* which forms at the same time the one electrode of the current. The second electrode *e* is insulated from *abc* by means of glass. The Wollaston-wire is fastened between *b* and *d*.

The dimensions are so chosen, that a pressure of 1 barye can be measured with greath accuracy. This is the case when the diameter of the wire is small compared to the mean distance described by the molecules since their last collision: for as long as this condition is satisfied, the loss of heat by the wire may be taken approximately proportional to the density (or the pressure) of the gas. Owing to a deviation from proportionality, which is due to the heat flowing off at the ends of the wire, a calibration is required. For this purpose the pressure was determined by means of the set of pipettes referred to before. The loss of heat is measured as follows. The wire forms one of the arms of a Wheatstone bridge (fig. 4); the corresponding arm has a resistance approximately equal to that of the wire, when it is heated to the definite temperature, which has been chosen with a view to the sensibility (in our case 86 degrees above 20° C.): it is kept at this temperature by regulating the main current. The two other arms have equal resistance (chosen in connection with the galvanometer resistance). The P. D. at the ends of a portion of one of these resistances is measured with a potentiometer free of thermo-effects: this gives the necessary data for the computation of the loss of heat.

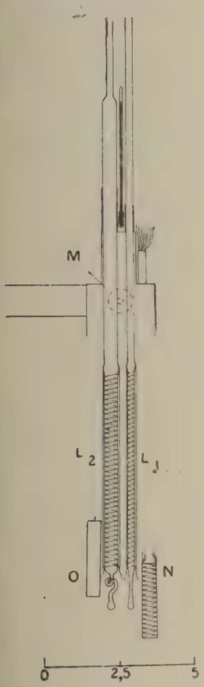

Fig. 5.

The calibration was carried out with the set of pipettes mentioned above. Fig. 5 gives the two vapour pressure tubes. They were partly double-walled; the walls are sealed together at the top and free at the bottom. Where the external tube ends, the inner tube becomes narrower and is bent round in a spiral finishing up in a small bulb; this bulb is placed at the level of the middle of the thermometer. In the space between the two walls of the tube a wire is inserted which can be electrically heated, so as to secure, that the bulb is the coolest place of the vapour pressure tube. The object of the spiral is to compel the molecules which come in from above to collide a number of times with the wall before reaching the bulb. That part of the tube cannot contribute to the thermal molecular pressure, as it is practically at the same temperature over its entire length.

We have made a series of observations for carbon dioxide with this apparatus ¹).

We confine ourselves here to those measurements which give at the same time a check on the last measurements with the absolute manometer contained in Table 2. The results were as follows:

TABLE III.

Vapour pressure of carbon dioxide at about —168°.

Temp. $T - 273°.09$ K	Pressure in baryes.	Vapour pressure in baryes.
	Vapour pressure tube I $2\,R = 1.57$ cM.	
—168.82	1.222	0.806
	Vapour pressure tube II $2\,R = 0.563$ cM.	
—168.82	1.288	0.797
—167.04	2.098	1.313

The last value will be seen to agree well with those obtained with the absolute manometer, while the first appears a little too high. We are uncertain as to the cause of this difference: most probably it is due to an uncertainty in the temperature with the absolute manometer.

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¹) The measurements at higher temperatures are dealt with in the next communication: S. Weber The vapour pressures of carbon dioxide between —140° C. and — 160° C.

It is of special interest to compare these observations with NERNST's formula. The fourth column of Table II contains the pressures according to this formula, calculated with the constants which FALCK [1]) has determined with the data at his disposal. FALCK found the following expression:

$$\log p = -\frac{6000}{4.571} \cdot \frac{1}{T} + 1.75 \log T - \frac{0.009983}{4.571} T + 3.1700$$

where p is the pressure in atmospheres.

The correspondence will be seen to be satisfactory considering the degree of accuracy of the observations. It does not look as if the constants could be materially improved.

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[1]) FALCK: Physik. Zeits. 1908, p. 433

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 137ᶜ.

SOPHUS WEBER. Vapour pressures of substances of low critical temperature at very low reduced temperatures. II. The vapour pressure of carbon dioxide in the range from — 140° C. to about — 160° C.

(*Translated from : Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **27 September 1913**, p. 380—389.)

Eduard IJdo — Printer — Leiden.

SOPHUS WEBER. — *Vapour pressures of substances of low critical temperature at very low reduced temperatures.* II. *The vapour pressure of carbon dioxide in the range from* — 140° C. *to about* — 160° C.

§ 1. In these measurements the heated-wire manometer described before was used [1]: it was calibrated by the aid of a set of pipettes as shown in fig. 1. The manometer is sealed to the vessel P_2 at J and is placed, together with P_1 and P_2 in a waterbath, in which a temperature of about 20° C. is maintained by means of a thermostat. This temperature is read on a mercury thermometer. The electric connections are the same as in fig. 4 of the first paper. In order to keep back mercury vapour or other vapours which might originate in P_2 the tube I the volume of which is only 1 % of the whole volume was placed in alcohol cooled to about —100° C. by the aid of liquid air. In a high vacuum the vapours given off by the grease of the stopcocks will be condensed in I. I have tried to prevent this flow of vapours to I while retaining the taps by interposing at G and H glass valves as introduced by KAROVODINE in TÖPLER-HAGEN's mercury pump.

Fig. 2 shows one of these valves; a is a ground surface. Inside the glass tube a small piece of iron is fastened: without a current through the electromagnet M the communication is open to the gas; when the current is closed the vapours can only diffuse through the narrow interstices left open at a. The measurements seem to confirm that by the use of these valves a better vacuum may be obtained.

The calibration was performed in the following manner. By means of the high-pressure taps D and C some carbon dioxide was taken from the cylinder A containing carbon dioxide which had been thoroughly dried and distilled several times. This gas was solidified in E by means of liquid air and subsequently strongly exhausted with a GAEDE-pump. It was then distilled into pipette p_1 and the pressure read with the manometer F. The pipettes P_1, p_2 and P_2 which communicated with the heated-wire

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[1] H. KAMERLINGH ONNES and SOPHUS WEBER. Comm. No. 137*b* (June 1913).

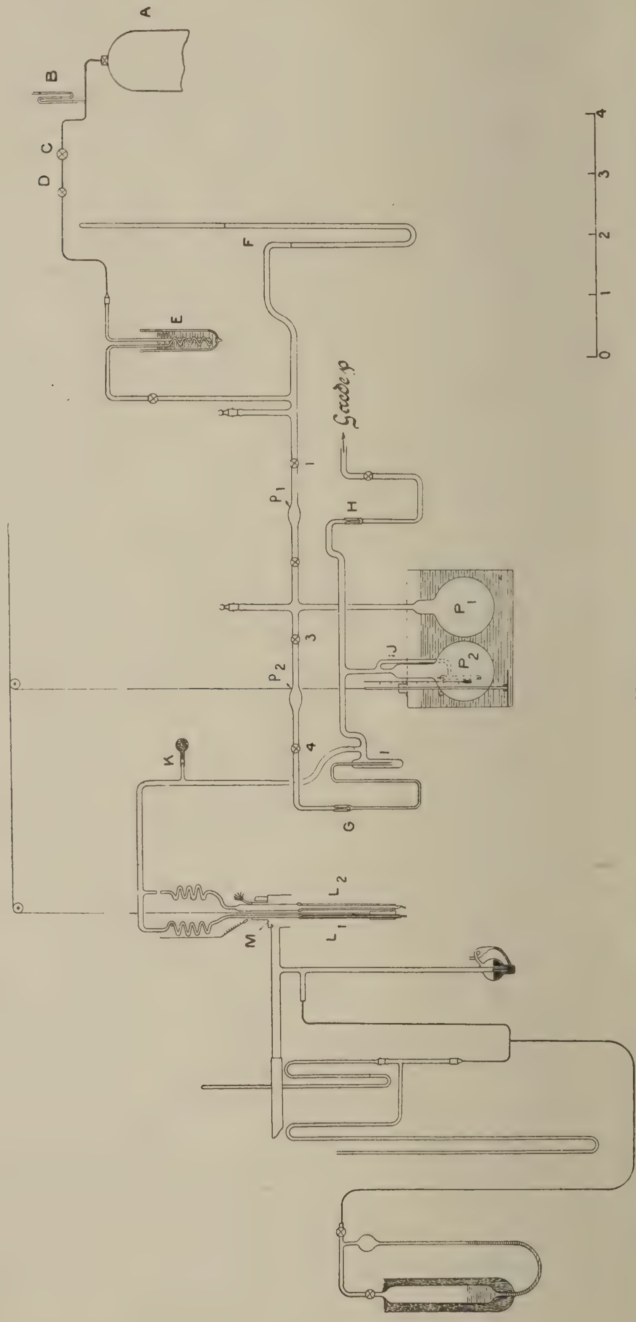

Fig. 1.

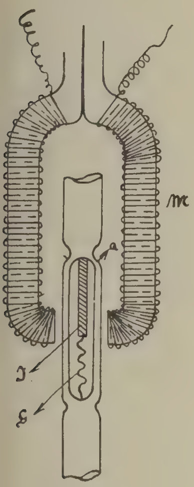

Fig. 2.

manometer were evacuated and the vacuum was measured with the aid of this manometer which had been previously compared with an absolute manometer. The gas in p_1 was then distributed over p_1, P_1 and p_2. If stop-cock 3 is now closed and 4 opened, the gas in p_2 is distributed over p_2 and P_2 by which the pressure in P_2 increases by a known amount. By connecting p_2 with P_1 and with P_2 successively the pressure in P_2 again increases by an amount which is known at least if the dimensions of the apparatus are known. They were:

$p_1 = 13.997$ cM^3
$P_1 = 2108.15$ „
$p_2 = 13.464$ „
$P_2 = 2555.7$ „

Each time when the pressure had been raised by a known amount the loss of heat of the WOLLASTON-wire under definite conditions was measured. The following table may serve as an instance of the calibration: q is proportional to the loss of heat per second and p is the pressure in baryes computed by means of the system of pipettes. The initial pressure is taken as zero in the table: in reality it amounted to 0.029 baryes.

TABLE I

p	q
0.000	0.6731
5.059	0.8019
10.099	0.9292
15.120	1.0551
20.122	1.1804
25.106	1 3044
30.070	1.4279
35.016	1.5305
39.943	1.6724
44.851	1.7932
49.740	1.9132
54.611	2.0332
59.464	2.1522

§ 2. After the calibration was completed the manometer was put into connection with a vapour pressure tube. This tube was of the form described in the previous communication. The measurements were conducted in the following manner. The apparatus was first exhausted as far as possible and was allowed to stand for some days, until the walls did not give off any more air. The vapour pressure tube which was placed in a cryostat together with a thermometer and a stirrer was then successively surrounded by ethylene, methane and oxygen and the vacuum was measured at temperatures between —130° C. and — 180° C. Carbon dioxide was then distilled into the apparatus and the vapour pressure measured at a series of temperatures. The difference between the two readings at each temperature after correcting for the thermal molecular pressure gives the vapour pressure of carbon dioxide.

In order to be able to obtain the corrections for the thermal molecular pressure it is necessary to work with different tubes suitably chosen. In this investigation two tubes were used, tube I with a diameter of 1.75 cm. and tube II of 0.563 cm.

The results of the measurements are contained in table II:

TABLE II.

	Pressure				
Temp. T—273.09	Measured tube I	Measured tube II	I corr.	II corr.	Calculated according to Nernst
—134.67	1430.6	1430.6	1430.6	1430.4	1429.9
136.78	1001.2	1002.8	1001.2	1002.5	1002.0
138.69	720.0	720.6	719.9	720.2	719.3
140.63	509.2	510.8	509.1	510.2	508.7
143.07	324.7	323.9	324.6	323.1	324.2
145.44	207.0	204.2	206.8	203.1	206.70
148.27	117.72	119.7	117.42	118.0	117.30
151.46	48.42	50.30	47.90	47.86	47.84
155.00	28.33	30.65	27.70	28.21	27.56
158.55	12.92	14.09	12.34	12.12	12.00
159.72	9.82	10.72	8.66	8.94	9.015
161.39	6.74	7.50	5.85	6.00	5.942
163.19	4.43	4.99	3.75	3.77	3.737
164.03	3.63	4.07	3.03	2.98	2.993
168.83	1.222	1.288	0.806	0.797	0.790

The first column contains the temperature as determined by means of a calibrated Pt.-thermometer. The second and third give the results of the measurements with the two tubes expressed in baryes, the fourth and fifth the same numbers after correcting for the thermal molecular pressure For the measurements between —150° and —162° these corrections are somewhat uncertain, as they have been determined experimentally for hydrogen and oxygen only. Moreover the tubes had not been chosen as favourable as possible, as will be clear from the following.

The corrections are calculated by means of KNUDSEN's formulae[1]). In the previous communication it was shown that with the degree of accuracy of our measurements these formulae may be considered as correct, if the region where approximately $1 < \frac{\lambda}{2R} < 10$ is excluded. If BREITENBACH's observations on the viscosity of carbon dioxide are extrapolated by means of SUTHERLAND's formula [2]) it may be concluded that the corrections cannot be computed in the range between 25 and 3 baryes for the wide tube and between 75 and 8 baryes for the narrow tube. Supposing that the mean free path is known with sufficient accuracy it will be seen that between 25 and 8 baryes there is a range for which the correction cannot be calculated. An additional tube of say 1 mm. diameter ought to have been used.

It appears further that below 3 baryes there is a range of pressures, where the correction can be found for both tubes With the formula which holds for this range the mean free path may be determined by eliminating the unknown vapour pressure The result of this calculation is found to agree within the limits of accuracy of the observations with the mean free path as calculated with SUTHERLAND's formula In table II this shows by the close agreement between the vapour pressures under I corr. and II corr.

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[1]) MARTIN KNUDSEN. Ann. der Phys. 31 (1910), p. 205, 633; 33 (1910), p. 1435.

[2]) The extrapolation by means of SUTHERLAND's formula is probably allowable in this case, as the range of reduced temperature is comparatively small. Over larger ranges of reduced temperature SUTHERLAND's formula does not appear to be applicable (H. KAMERLINGH ONNES, C. DORSMAN and SOPHUS WEBER, Comm N⁰. 134*a* March 1913).

The conclusion seems therefore justified that the mean free path of carbon dioxide is known with sufficient accuracy at these temperatures, and that the corrections may be deduced by means of Knudsen's formulae with the exception of the range between 25 and 8 baryes

Leaving this range out of account in the mean time we will now discuss the formulae for those ranges where in our opinion they are still applicable.

(1) $\frac{2R}{\lambda} > 10.$

In this range we use the following formula theoretically deduced by Knudsen.

$$\frac{dp}{dT} = \frac{0.00139 \dfrac{1 + \dfrac{c}{273}}{1 + \dfrac{c}{T}} \dfrac{\eta_0}{\sqrt{\rho_0}} k_1}{R + 32.07 \dfrac{\left(1 + \dfrac{c}{T}\right)\sqrt{\rho_0}}{\left(1 + \dfrac{c}{273}\right)\eta} R^2 \dfrac{p}{T} k_2} \quad . \quad . \quad . \quad . \quad (I)$$

The meaning of the symbols is the same as in Knudsen's paper. According to the theory the constants k_1 and k_2 are independent of the nature of the gas. Experimentally this formula has been confirmed for hydrogen and oxygen, and k_1 and k_2 appear actually to be independent of the nature of the gas. The equation which may be integrated in a fairly simple manner looses its validity for small values of $\frac{2R}{\lambda}$. For carbon dioxide the formula was used with the values of k_1 and k_2 which were found from the measurements with hydrogen and oxygen. As shown by Table II the numbers under I corr. and II corr. agree well with each other which may be looked upon as a partial confirmation of the underlying suppositions. Fig. 3 gives a graphic representation of $\frac{dp}{dT}$ according to the different formulae. The abscissae give the pressures in baryes, the ordinates $\frac{dp}{dT}$ for the tube with

$2R = 0.563$ cm. Curve *I* represents the relation according to formula *I*. For the corrections the formula has not been used, when

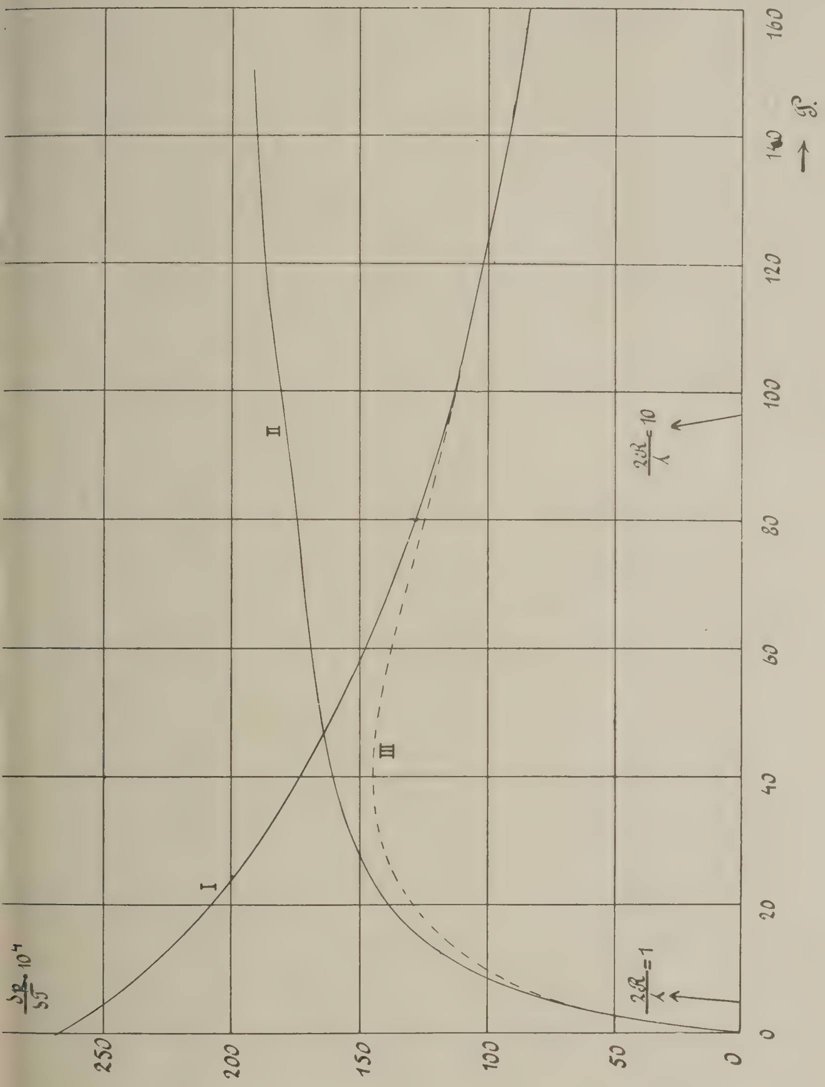

Fig 3.

$\frac{2R}{\lambda} < 10$; it depends, however, on the degree of accuracy required, where the limit has to be taken.

(2) $\frac{2R}{\lambda} < 1$.

In this case the following formula was used for $\frac{dp}{dT}$:

$$\frac{dp}{dT} = \frac{1}{2} \frac{1}{1 + \frac{2R}{\lambda}} \frac{p}{T} \tag{II}$$

where p and λ are connected by the relation $p \, . \, \lambda = \text{const.}$; this constant is determined by the viscosity corresponding to the temperature T.

For sufficiently small values of $\frac{2R}{\lambda}$ the formula reduces to

$$\frac{dp}{dT} = \frac{1}{2} \cdot \frac{p}{T} \quad \text{or after integration} \quad \frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}.$$

The limit for the application of formula *II* has been taken at $\frac{2R}{\lambda} = 1$, which gives about the same accuracy as in the former case. The relation between p and $\frac{dp}{dT}$ according to formula *II* is also given in Fig. 3.

(3) $1 < \frac{2R}{\lambda} < 10$.

In this region the formulae can probably only be used as rough approximations. Curve *III* in fig. 3 has been obtained by reducing the observations for hydrogen and oxygen to carbon dioxide by means of the law of corresponding states. The values given by *III* have been used in this range for calculating the corrections. The results under I corr. and II corr. agree fairly well with each other. The observations are, however, not sufficient to draw conclusions with regard to the value of thermal molecular pressure in this intermediate region.

This region has, therefore, not been sufficiently studied as yet and new measurements in this range would be of the greatest interest.

In table II column 5 under "calc. according to NERNST" the pressures are given calculated by the aid of NERNST's formula.

In the former paper use was made of the formula with the values of the constants found by FALCK [1]), viz.

$$\log p = -\frac{6000}{4.571}\cdot\frac{1}{T} + 1.75 \log T - \frac{0.00913}{4.571}\,T + 3.1700 \quad (I)$$

In order to obtain a satisfactory agreement at higher pressures the constants had to be slightly modified as follows

$$\log p = -\frac{6007.9}{4.571}\cdot\frac{1}{T} + 1.75 \log T - \frac{0.009008}{4.571}\,T + 3.1700 \quad (II)$$

p is here expressed in atmospheres.

The coefficient of $\log T$ and the chemical constant are unchanged, and the other two constants have been only slightly altered. This alteration can have no influence on FALCK's theoretical deductions. The very low vapour pressures which we measured before with the absolute manometer are also unchanged, as the term proportional to T has but little influence in that region. In that case NERNST's formula reduces to the vapour pressure formula according to KIRCHHOFF-RANKINE-DUPRÉ [2]).

It can hardly by expected that formula *II* should give good agreement at temperatures much higher than those given in table II. At higher temperatures FALCK finds greater deviations which, however, he considers to be due to errors of observation. I have made only one measurement at temperatures higher than those given in table 2.

Temperatures	p	Calc. by form. *II*
$T - 273.09$	cm. Hg	
— 129.29	0.3943	0.2536
— 129.28	0.3948	0.2539

Although this measurement is the only one it may be considered sufficient together with the observations by ZELENY and SMITH [3]) to infer a considerable deviation from the formula at this temperature.

In conclusion I am glad to record my gratitude to Prof. H. KAMERLINGH ONNES for his kind assistance and his ever ready interest in my work.

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[1]) F. FALCK: Phys. Z. S. 1908, p. 433.

[2]) H. KAMERLINGH ONNES und W. H. KEESOM: Die Zustandsgleichung. Suppl. N⁰. 23 p. 300.

[3]) ZELENY u. SMITH. Phys. Z. S. p. 667, 1906.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 137^{d}.

H. KAMERLINGH ONNES and W. H. KEESOM. On the measurement of very low temperatures. XXIII. The vapour pressures of hydrogen from the boiling point down to near the triple-point.

(*Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **27 September 1913**, p. 389—393.)

Eduard IJdo — Printer — Leiden.

H. KAMERLINGH ONNES and W. H. KEESOM. *On the measurement of very low temperatures. XXIII. The vapour pressures of hydrogen from the boiling point down to near the triple-point.*

(Communicated in the meeting of June 28, 1913).

§ 1. The vapour pressures of hydrogen between the boiling point and the triple-point have been determined by DEWAR [1]) and by TRAVERS and JAQUEROD [2]). The value, which was obtained at Leiden for the heat of vaporization of hydrogen at the boiling point [3]), differed, however, appreciably from the values which follow with the aid of the CLAPEYRON-CLAUSIUS formula from the measurements of the vapour pressures mentioned above, taking into account the compressibility of hydrogen vapour according to the measurements of KAMERLINGH ONNES and W. J. DE HAAS [4]). A deviation between the AVOGADRO scale of temperatures fixed by the aid of the gas thermometer, and the KELVIN scale of temperatures [5]) of such an amount as would be indicated by the difference between these results may be considered improbable [6]).

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[1]) J. DEWAR. Proc. Roy. Soc. London, A. 76 (1905), p. 336.

[2]) M. W. TRAVERS and A. JAQUEROD. Phil. Trans. (A) 200 (1902), p 155.

[3]) For a preliminary report see: W. H. KEESOM, Handelingen 13de Ned. Nat en Geneesk. Congr. 1911, p. 181, these Communications N^0. 137*e*. According to a later calibration of the ampère- and voltmeter, which were used, with the aid of a water calorimeter the values given there are to be diminished by an amount of $2^0/_{00}$. Hence the value found with the smallest velocity of vaporization for the heat of vaporization of hydrogen at the boiling point (more accurately at an average pressure of 751.5 mm.) becomes 110.2 cal_{15}. The vapour pressures according to DEWAR lead to the value 106, whereas those according to TRAVERS and JAQUEROD give a still smaller value.

[4]) H. KAMERLINGH ONNES and W. J. DE HAAS. Comm. N^0. 127*c* (May 1912).

[5]) Cf. H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. N^0. 23, § 82*a*.

[6]) This view is supported by the fact, that according to KEESOM, Suppl. N^0. 30*a* § 4, the application of the quantum-theory with the introduction of the zero-point energy to the molecular translatory motion for a gas at such a density that the dimensions and the mutual attraction of the molecules need not to be considered, leads to an appreciable divergence from the equation $p = RT/v$ at extremely low temperatures only.

It seemed therefore of interest to undertake a new determination of the vapour pressures of hydrogen in the region mentioned.

§ 2. The measurements were made with the aid of a vapour pressure apparatus as described by KAMERLINGH ONNES and BRAAK in Comm. N⁰. 107*a* (May 1908) Pl. I apparatus *A*.

The temperatures were measured ¹) with the aid of the platinum resistance thermometer ²) Pt_I. We could avail ourselves of a more recent comparison (May 1913) of Pt_I with the hydrogen thermometer performed at 6 points, regularly distributed over the range from the boiling point to near the triple-point, by KAMERLINGH ONNES and HOLST in their research concerning the comparison of the scales of the hydrogen and the helium thermometers. The corrections ³) to the KELVIN scale for this hydrogen thermometer ($p_{0^\circ C} = 120$ c.m.) (+ 0.14 down to — 253°, + 0.15 for — 254° and — 255°, + 0.16 for — 256°, + 0.17 for — 257°, + 0.18 for — 258°, + 0.20 for — 259°) were deduced down to — 257° from the corrections of the scale of the international hydrogen thermometer found for this region by KAMERLINGH ONNES and W. J. DE HAAS, Comm. N⁰. 127*c* (June 1912), those for the lower temperatures were calculated according to the research of KAMERLINGH ONNES and HOLST mentioned above.

75.95 cm. of mercury was adopted as the international atmosphere ⁴) at Leiden.

§ 3. The results are given in the following table ⁵).

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¹) We gladly record our cordial thanks to Mr. G. HOLST for the aid afforded to us by performing these temperature measurements.

²) The bath was kept constant within $^1/_{300}$ of a degree.

³) The corrections given here differ somewhat from those given in the Dutch edition of this paper, in accordance with the results of the research of KAMERLINGH ONNES and HOLST mentioned in the text.

⁴) Cf. H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. N⁰. 23, Einheiten *a*.

⁵) The numbers given in this table, and those derived from it further on in this paper differ slightly from those given in the Dutch edition in accordance with the slightly altered values of the correction to the KELVIN scale (cf. note 3) and an improved calculation of the temperatures.

Erratum Communication N^0^. 137.

p. 40 line 15 from the top: for „$p_{0°C.} = 120$ cm." read „$p_{0°C.} = 119$ cm."

Vapour pressures of hydrogen.

θ Kelvin degrees	p internat. cm. of mercury	$p_{calc.}$	$p_{obs.} - p_{calc.}$	$\theta_{obs.} - \theta_{calc.}$	pressure of the bath	
—252.63	78.91	79.01^5	— 0.10^5	0.00	78.34	much liquid
[252.66	77.97	78.33	— 36	— 2]	78.15	» »
253.76	56.07	56.02	+ 5	0	55.62	» »
255.12	35.17	35.10	+ 7	+ 0^5	35.26*	» »
255.17	34.53^5	34.46	+ 7^5	+ 0^5	34.18	» »
256.08	24.16	24.20	— 4	0	24.00*	» »
256.08	24.19	24.20	— 1	0	24.47^5*	little »
256.09	23.99	24.11	— 12	— 1	23.77	much »
257.19	14.97	14.95	+ 2	0		» »
258 31	8.60	8.60	0	0	8.53	» »

The difference 0.03 cm. between the values of the pressure found at — 256°.08 with much and with little liquid corresponds to a difference in temperature of 0.003 of a degree and lies within the limits of accuracy; moreover it is in a direction opposite to that which would follow from the supposition of an increase of pressure at condensation; hence there is no evidence of an influence of admixtures.

The pressure in the cryostat has also been given in the table (column 6). The manometer, on which this pressure was read, was connected to a side tube of the cover of the cryostat; this cover had at this place the same width as the cryostat glass. At the pressures marked with an * the tube, which formed the connection with the manometer, was continued within the cryostat by a glass tube which reached down into the liquid ^{1}). By this means we obtained the result that the vapour pressure was measured at a liquid surface where no continued vaporization

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^{1}) In order to have a better guarantee that the pressure which is read belongs to the temperature of a definite place in the liquid, this tube might be surrounded by a heat conducting tube reaching above the liquid surface, as in the vapour pressure apparatus (cf. N^0. 107*a*, Pl. I).

(and hence cooling of the upper layers) takes place. The influence of this can be clearly seen: in the observations without * for all but one[1]) the pressure of the bath was found smaller than that in the vapour pressure apparatus, for the observations with * just the reverse is the case. On the average in these latter observations the difference is moreover smaller. The temperature difference which corresponds to the largest pressure differences is 0.03 degrees. If for the measurement of the temperature in liquid hydrogen one is satisfied with this degree of accuracy, it is sufficient for the purpose to measure the pressure in the cryostat in the way indicated.

As the triple-point could not be properly observed in the vapour pressure apparatus, for determining the triple-point temperature the temperature of the bath was read when the first crystals became visible in the latter The indication of Pt_I then became constant; 1.415 Ω was read. Extrapolation (over 0.8 degree) of the calibration curve of Pt_I gives for the triple-point temperature — 259°.14 C in KELVIN degrees = 13°.95 K. The pressure of the bath was 5.07 cm. at this point.

§ 4. The curve which represents log p as a function of $\frac{1}{T}$ is slightly concave upwards[2]). In the 3rd column the values are

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[1]) For this one, placed between [ ], the experimental data indicate that in the vapour pressure apparatus temperature equilibrium probably was not yet arrived at. [Added in the translation.]

[2]) The measurements of TRAVERS and JAQUEROD give a log p, T^{-1}-curve which is slightly *convex* upwards. The following table gives some numbers which enable a comparison with the data by TRAVERS and JAQUEROD.

p internat. cm. of mercury	T KELVIN-scale (K.O. and K.)	T*) KELVIN-scale (T. and J.)
76	20.33	20.33
35	17.96	17.90
10	15.07	15.07

*) Temperatures measured with a hydrogen thermometer, corrected by us to the KELVIN scale with corrections derived from the numbers given in § 2. [Added in the translation].

given of p calculated from a WREDE-RANKINE-KEESOM formula [1] [2]:

$$\log p_{\text{in cm.}} = 4.6063 - \frac{58.40}{T} + \frac{61}{T^2} \quad . \quad . \quad . \quad . \quad . \ (1)$$

The 4th column gives the differences of the observed values and the values calculated from (1), the 5th column the corresponding differences in temperature.

From (1) follows for the boiling point: 20.33° K. = — 252.76° C. [3]

Extrapolation by (1) would give 5.41 cm. for the pressure corresponding to the triple-point temperature found in § 3 (with extrapolation of the calibration curve of Pt_I). The double extrapolation makes this value somewhat uncertain; it can in the mean time be regarded as a confirmation of the value found by KAMERLINGH ONNES and BRAAK [4]).

§ 5. The heat of vaporization of hydrogen at a pressure of 75.15 cm. calculated according to CLAPEYRON-CLAUSIUS from (1), if for calculating v_{vap} the value $B_{A(71)}$ is taken from KAMERLINGH ONNES and W. J. DE HAAS, Comm. N⁰. 127*c*, with v_{liq} after KAMERLINGH ONNES and CROMMELIN, Comm. N⁰. 137*a*, becomes:

$$\lambda = 105.5 \ \text{cal}_{15}.$$

This value [5]) is smaller than that found by direct measurement at the smallest velocity of vaporization [6]): 110.2 It is possible that this result indicates that the precautions taken to prevent condensation of the vaporized hydrogen within the calorimeter have not been sufficient. In fact at a velocity of vaporization twice as great as that at which the value mentioned above was found smaller values were obtained, *viz.* 108.5 and 109.3 at 76 1 and 77.75 cm. pressure respectively.

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[1]) Cf. H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. N⁰. 23, § 83 *g*.

[2]) Cf. p. 40 note 5.

[3]) This number coincides with that derived from the measurements of TRAVERS and JAQUEROD, cf. p. 42 note 2. [Added in the translation].

[4]) H. KAMERLINGH ONNES and C. BRAAK. Comm. N⁰. 95*e* (Oct. 1906). According to (1) to the pressure 5,38 cm. found there a temperature of 13°.94 K. corresponds.

[5]) It may be noticed that this value nearly coincides with that calculated from the vapour pressure measurements of DEWAR (cf p. 39 note 3). The difference which shows the value derived from the vapour pressure measurements of TRAVERS and JAQUEROD (cf. p. 39 note 3) is due to the diverging course of their vapour pressure curve, cf. p. 42 note 2. [Added in the translation.]

[6]) Cf. p. 39 note 3, and further Comm. N⁰. 137*e*.

COMMUNICATIONS

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BY

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N°. 137e.

W. H. KEESOM. The heat of vaporization of hydrogen.
(*Translated from: Handelingen van het* 13de *Ned. Nat. en Geneesk. Congres,* **April 1911,** p. 181—186).

Eduard IJdo — Printer — Leiden.

W. H. KEESOM. *The heat of vaporization of hydrogen.*

This is the first of a series of investigations on the calorimetry at very low temperatures in the Leyden cryogenic laboratory.

Calorimetric determinations at the temperatures which are obtained with liquid hydrogen have been published so far [1]) by DEWAR only. This scientist measured the heat of vaporization of hydrogen boiling under atmospheric pressure, and the average specific heat of diamond, graphite, ice and brass over a temperature range down to the boiling point of hydrogen Further we may mention P. CURIE and DEWAR's determination in the hydrogen calorimeter of the development of heat by radium bromide, and DEWAR's measurement of the heat developed in the absorption of hydrogen and helium by char-coal.

Prof. KAMERLINGH ONNES and I resolved to determine in the first instance the heat of vaporization of hydrogen at atmospheric as well as at reduced pressure. Determinations of the specific heat, especially of metals, would follow.

For measuring the heat of vaporization a quantity of heat was supplied by means of an electric current under continuous stirring to a quantity of liquid hydrogen contained in a vacuum vessel, which was surrounded by another vacuum vessel with liquid hydrogen. The vaporized hydrogen was collected and measured. To be able to apply the correction for the quantity of hydrogen which in the experiment vaporized in consequence of the heat supplied by radiation and conduction from outside, two other experiments without electric current were made, one immediately before, and one immediately after it [1]).

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[1]) As far as I knew at the time of the reading of this paper (April 1911). Since then (*i. e.* between the reading of the paper and the printing of these proceedings in Dutch) I have become acquainted with measurements of the specific heat of different substances down to some degrees above the boiling point of hydrogen by W. NERNST, Berl. Sitz. Ber. 1911 (published March 16), p. 306, and by W. NERNST and F. A. LINDEMANN, ibid. p. 494 (published May 4).

The hydrogen vaporized in these last mentioned experiments was collected in evacuated glass vessels of about 2 litres capacity, the hydrogen vaporized in the experiment with electric current in two steel vessels, which were also evacuated and which together have a capacity of about 45 litres.

The capacities of the glass vessels were measured with distilled water, those of the steel vessels and the connections (dead spaces) were measured volumenometrically. The pressure of the gas collected in them was read on an closed mercury manometer with the aid of a cathetometer. For measuring the temperature of the gas the steel and glass vessels were packed together with thermometers in wool and cotton-wool.

The heat-supply was measured electrically with the aid of Weston precision- am- and voltmeters, whereas the time was accurately adjusted to an even number of seconds by a clock with Hohwü registering arrangement, which closed or opened the circuit at moments enclosing an even number of seconds to be chosen at will [2]).

In a determination with hydrogen, in which the pressure inside the vaporization vessel was 777.5 mm., the current about 0.275 A. and the tension about 11.1 V., a quantity of gas was collected of 70.5 ml. in the first experiment without current (230 secs.), of 18439 ml in the experiment with current (270 secs), and of 123.3 ml in the second experiment without current (240 secs.).

In this case the collecting of the hydrogen fòr the experiment with the current was begun 10 secs. before the closing, and was continued 20 secs. after the opening of the circuit.

From the data given it follows that the development of hydrogen in consequence of the heat supply by radiation and conduction during the experiment with the current, calculated from the first experiment without the current, differed from that calculated from the second experiment without the current considerably less than 1 $^0/_0$ of the total amount. This was always the case except in the measurement at the lowest pressure.

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[1]) Some preliminary experiments with liquid air were made by Mr. J. Clay.

[2]) We record our cordial thanks to Mr. G. Holst, who made these manipulations and took these readings.

As a test of the method and for practise with the apparatus some determinations of the heat of vaporization of oxygen were made.

We found [1]:

Febr. 24	I	pressure:	760 mm.:	51.3 cal_{15}. (weight $\frac{1}{2}$)
„ „	II	„	759 „ :	50.4 „
„ „	III	„	760 „ :	50.5 „

The heat of vaporization of oxygen has been determined by SHEARER, ESTREICHER, DEWAR and ALT. I leave out of account some determinations on the vaporization of air rich in oxygen.

The most reliable are the results obtained by

DEWAR 51.15
and especially those by ALT 50.92 at 760 mm.

Our results differ from the latter by less than 1 $^0/_0$, from the former a little more [2].

For hydrogen we found [3])

		pressure	heat of vaporization	
Febr. 27	I	761 mm.	108.5 cal_{15}	
„ „	II	777.5 „	109.3 „	
April 13	I	416 „	109.6 „	[4]
„ „	II	422 „	111.4 „	
„ „	III	121 „	113.2 „	

The value obtained here for the heat of vaporization of hydrogen under atmospheric pressure is considerably smaller than the value given by DEWAR [1]), *viz.* 123.

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[1] On account of a test of the ammeter and voltmeter with the aid of a water calorimeter accomplished after the publication of the dutch edition the results for the heat of vaporization given in that edition have been diminished here by 2 $^0/_{00}$.

[2] Since then H. BARSCHALL, Z.S. f. Elektrochemie 17 (1911), p. 345, has published measurements which give 51.3.

[3] Cf. note 1.

[4] The corrections which are to be applied for the quantity of vapour which occupies the place of the vaporized liquid have been calculated for this measurement and for the next two with extrapolated values of the virial coëfficient B (cf. further on in the text).

If in the boiling small drops are carried away by the vaporized hydrogen a value which is too small may be found for the heat of vaporization In order to estimate this source of error it is desirable to perform a series of observations at a smaller velocity of vaporization. In the mean time it is difficult to suppose that the divergence between DEWAR's result and ours could be explained by this circumstance [2]).

Our result is supported by the following.

Assuming $\frac{dT_{\text{coëx.}}}{dp_{\text{(in mm.)}}} = 0.00442$ at $p = 1$ atm. according to DEWAR, with $T = 20.25$, and in calculating v_{vap} taking account of the deviation from BOYLE-GAY-LUSSAC's laws by making use in the equation

$$pv = A + \frac{B}{v}$$

of the value of B obtained by KAMERLINGH ONNES and W J. DE HAAS (Comm. N°. 127*c*), CLAPEYRON-CLAUSIUS's formula

$$\lambda = T \frac{dp_{\text{coëx.}}}{dT} (v_{\text{vap.}} - v_{\text{liq.}})$$

gives $\lambda = 106.4$. The value $\frac{dT_{\text{coex.}}}{dp_{\text{(in mm.)}}} = 0.0048$ according to TRAVERS and JAQUEROD gives a still smaller value for the heat of vaporization. For a reliable calculation of the value of λ from

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[1]) J. DEWAR. Proc Roy. Soc. A 76 (1905), p. 325.

[2]) Before the printing of the Dutch edition of this paper measurements were made with a velocity of vaporization half of that of Febr. 27. They gave:

April 26 I	747 mm.	110.2
„ „ II	756 „	110.2.

In this translation I can add that from determinations of the vapour pressures of hydrogen by H. KAMERLINGH ONNES and W. H. KEESOM (Comm. N°. 137*d*) follows that these values, and even those given in the text for about the atmospheric pressure, are still somewhat too high. This may possibly be ascribed to the precautions for preventing the vaporized hydrogen recondensing inside the vaporization vessel not having been entirely sufficient.

the vapour pressures for hydrogen it is necessary to obtain a better knowledge of the vapour pressure law of this substance.

As regards the way in which DEWAR comes to his higher value for the heat of vaporization of hydrogen it appears that this scientist calculated the quantity of heat furnished to the hydrogen by adopting for the specific heat of lead, which he dropped in weighed quantities into his hydrogen calorimeter either at room temperature or cooled in liquid air, values which were obtained by a linear extrapolation from those which are valid for higher temperatures. In connection with EINSTEIN's theory of the specific heat and after what NERNST's determinations at low temperatures have already shown, this must be considered very dangerous. Now that the heat of vaporization of hydrogen has been measured directly one would prefer to derive from DEWAR's measurements the specific heat of lead at these very low temperatures. However the determinations in which lead of room temperature was dropped into liquid hydrogen then give values which do not agree with those derived from determinations in which the lead was cooled beforehand in liquid air.

Direct determinations of the specific heat of lead, and also of other metals are desirable in connection with EINSTEIN's theory, according to which at these low temperatures vibrators such as PLANCK assumes in his radiation theory, and which can only emit or absorb energy quanta of a definite magnitude determined by their frequency, are to be considered as the carriers of the atomic heat in solids and also with a view to the heat theorem advanced by NERNST and brought into connection with EINSTEIN's theory.

These determinations are all the more interesting now that KAMERLINGH ONNES has shown that presumably also the galvanic resistance of metals at low temperatures is determined by the energy of those vibrators.

A communication on measurements with an apparatus in which the temperature increase is determined, which a piece of lead at the temperature of liquid hydrogen undergoes when a measured quantity of heat is supplied to it, may be expected in the course of time.

TROUTON's constant becomes for oxygen (taking the boiling point at —183.0° C. according to KAMERLINGH ONNES and BRAAK) $\frac{\lambda_M}{T_{\mathrm{coex.}\, p\, =\, 1}}$ = 18.0, for hydrogen with the boiling point 20.25° on the hydrogen scale according to DEWAR: 11.0.

The average value for normal substances with higher values of T_k is 20.7.

We see here a consequence of the gradual deformation of the reduced characteristic surface as we proceed to substances with low critical temperature.

Finally we remark that the apparatus used for this investigation, now that the heat of vaporization of hydrogen has been determined, can be used as a hydrogen calorimeter for measuring at these temperatures the heat development of various processes, such as chemical ones, in so far as these can be realized at those very low temperatures, and hence, if on the other hand the maximum work of those processes is known, to test the relation of these two quantities as given by NERNST's heat theorem.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 138^a.

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J. P. KUENEN and S. W. VISSER. The viscosity of the vapour of normal butane.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **27 September 1913,** p. 336—343.)

EDUARD IJDO — PRINTER — LEIDEN.

J. P. KUENEN and S. W. VISSER. *The viscosity of the vapour of normal butane.*

For the determination of the viscosity of butane vapour RANKINE'S [1]) transpiration method was used; a method which is very simple and requires very little vapour, and in which the vapour comes into contact with glass and mercury only.

The apparatus consists of a long O-tube placed vertically and capable of being turned over on a horizontal axis. One arm of the O is capillary, the other one a wider tube The vapour is forced through the capillary by a falling drop of mercury in the wide tube. When the drop has arrived a the bottom of the tube, the apparatus is simply turned upside down, and the drop now drives the gas through the capillary in the opposite direction. The time is measured between the moments at which the mercury passes two marks on the fall-tube. The whole tube is mounted in a glass jacket, where the temperature is kept constant.

In order to be able to work with a long capillary without making the apparatus unwieldy by its length, a capillary is used which is twice bent round: hereby it becomes almost three times as long as the wide tube.

The apparatus is provided at the top and the bottom with side-tubes which serve for the purpose of cleaning and filling and are sealed off before the measurements. At both ends the tube has a slight enlargement for collecting the mercury.

When the tube is used for relative measurements, the formula to be used is

$$\eta_1 : \eta_2 = t_1 : t_2$$

where η_1 and η_2 are the viscosities of both vapours, t_1 and t_2 their times of flow.

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[1]) A. O. RANKINE, Proc. Roy. Soc. London A 83, 265, 516; 1910.

A correction has to be applied for gliding by means of the relation

$$\frac{\eta_1}{\eta_2}=\frac{t_1}{t_2}\frac{1+\frac{4\,G_1}{R}}{1+\frac{4\,G_2}{R}}=\frac{t_1}{t_2}\left\{1+\frac{4\,G_2}{R}\left(\frac{G_1}{G_2}-1\right)\right\}$$

where G_1 and G_2 are the mean free paths of the two vapours and R is the radius of the capillary. When $\frac{G_2}{R}$ is known, a rough approximation for $\frac{G_1}{G_2}$ is sufficient.

The kinetic theory gives $\eta={}^1/_3\,dG\,V$ and $p={}^1/_3\,d\,V^2$, where d is the density, V the square root of the mean velocity square, p the pressure. Eliminating V we find $\eta=\sqrt{{}^1/_3\,pd}\,G$ and therefore

$$\frac{G_1}{G_2}=\frac{\eta_1}{\eta_2}\sqrt{\frac{d_2\,p_2}{d_1\,p_1}}.$$

Critical velocity. Reynold's criterion for liquids also holds for gases [1]. For our viscosimeter, $\frac{Ddv}{\eta}=146$ for air (admissable limit is 2000) D was .0358 cm.; $d=.001293$; $\eta=.000181$; the volume 2.246 ccm.; the time of flow 57 seconds.

Correction for the capillary action of the mercury drop.

In consequence of the difference in curvature of the two surfaces of the mercury drop, a correction has to be made in the pressure which may be different for different gases and different temperatures. This correction was determined by Rankine by measuring the time of flow for several mercury drops of different length The relation between the mass m of the mercury and the time of fall t may be represented by the equation

$$m=a+\frac{b}{t}$$

where a is the unknown correction and b a constant, which is equal to the product of the corrected mass and the time. From a series of measurement with different m, the constants a and b may be calculated.

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[1] Ruckes, Ann. Phys. **25**, p. 983, 1908.

In order to avoid the use of different masses which involved opening, refilling and reclosing the tube, an attempt was made to determine the correction in a different manner. By dividing a given quantity of mercury into a train of drops which fall down together the capillary action is multiplied [1]). If the influence of each separate drop is the same, the correction must be proportional to the number of drops. Calling the number of drops x, RANKINE's equation becomes

$$m = xa + \frac{b}{t}.$$

a and b may thus be calculated from several measurements with different x, m being known. If m is taken unknown the ratios a/m and b/m may be found. Calling these ratios a_1 and b_1 the equation takes the form

$$a_1 x + b_1 \frac{1}{t} = 1$$

b_1 is thus the time for $x=0$ i.e. the time corrected for the influence of capillarity. According to this equation the graphical relation between x and $\frac{1}{t}$ should be a straight line.

In the application of this method some unexpected difficulties made their appearance.

To begin with the constants a and b were derived from three observations by RANKINE's method.

RANKINE's *method*	m	1.86	1.31	1.01	grms.
	t	57.1	84.5	114.2	seconds.

temp 14.5°.

These results give:

$$a = 0.160 \qquad b = 97.10.$$

The observations with air were now repeated by the drop-method.

Drop-method. 1st series.	m	1.09				
	x	1	2	3	4	5
	t	102.7	119.7	143.3	174.3	216.9

temp. 15.5°.

These points do not lie exactly on a straight line. The deviation is very small for the first three drops; the fourth point is too high and the fifth deviates still more in the same direction. The first two drops give

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[1]) By providing the wide tube with a small contraction on the inside of the curve near one of the bulbs, it is easy to divide the mercury column into two or more drops.

$$a = 0.135 \qquad b = 97.99.$$

As this result does not agree with the former result as regards a, a further investigation of the method was made with air after the completion of the observations with butane. In this case three quantities of mercury were taken, each of which was used in a different number of drops.

The results were als follows:

Drop-method. 2nd series.	x			1	2	3	
	m	2.11	t	49.0	54.4	62.0	temp. 19.8°.
	m	1.53	t	69.1	80.1	97.9	temp. 19.5°.
	m	1.06	t	103.6	129.9		temp. 19.5°.

From this set the influence of capillarity for one, two or three drops may also be calculated by RANKINE's method.

The first column gives $a = .121$ $b = 97.59$ for one drop.
„ second „ „ $a = .306$ $b = 98.31$ for two drops.
„ third „ „ $a = .533$ $b = 97.97$ for three drops.

The capillary effect per drop thus becomes:

.121 .153 .178.

it seems therefore to become greater as the number of drops increases.

The value of b is practically constant: the deviations are 0.4$^0/_0$ and remain below the errors of observation.

In the calculation by the drop-method (combination of the results in the same row) the third point appears to deviate downwards this time.

The first row gives for $x=1$ and $x=2$; $a=.192$ $b=94.1$ for $m=2.11$
„ second „ „ „ $a=.185$ $b=93.1$ „ 1.53
„ third „ „ „ $a=.179$ $b=91.6$ „ 1.06

The deviation from RANKINE's method of calculation is also in the opposite direction. The differences between the constants b are again much smaller than those between the a's.

The conflicting results of the two series of observation make it probable, that the differences between the two methods are accidental, due to small differences in purity of the mercury and of the walls of the tube. A further investigation is therefore desirable, as the drop-method, if found trustworthy, is much preferable to the method which depends on the use of different masses.

For high temperatures with air and for all temperatures with butane the drop-method was the only one that could be used. It appeared advisable to use the constants a and b as derived from the first series of the above determinations, because in the measurements at 100° and with butane the same quantity of mercury was used.

After the first series of determinations with air the time of flow for air in steam of boiling water was measured. In order to get an even temperature it was found necessary to admit steam by means of two flasks one at each end of the vapour jacket.

As mentioned above the constants a and b were determined according to the drop-method. As the results for air at ordinary temperature were found somewhat uncertain, the following results must also be considered to be only approximately correct.

Observations at 100.1°

$m = 1.09$

x	1	2	3
t	121.9	139.4	161.4

The deviation for $x=3$ is upwards.

From $x=1$ and $x=2$ follows

$$a=0.122 \qquad b=118.1$$

The constants a, .135 at 15.5° and .122 at 100°, thus appear to differ but little, compared to the differences between the observations with a different quantity of mercury.

We thus find

$$\frac{\eta_{100.1}}{\eta_{15.5}} = \frac{118.1}{97.99} = 1.205.$$

Corrected for gliding 1.205.

Breitenbach [1]) gives $\eta_{15} = .0001807$, Rankine [2]) $\eta_{15.5} = .0001803$; Markowski [3]) $\eta_{99.6} = .0002212$; Schierloch [4]) $\eta_{99.9} = .0002218$.

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[1]) Breitenbach, Ann. Phys. 5, 166; 1901.

[2]) A. O. Rankine l. c.

[3]) H. Markowski, Ann. Phys. (4) 14; 1904.

[4]) J. H. Schierloch, Diss. Halle 1908.

These values which have been selected from several which differ considerably give:

$$\frac{\eta_{100}}{\eta_{15.5}} = 1.228.$$

DETERMINATION OF THE VISCOSITY OF BUTANE VAPOUR.

The viscosimeter was connected to the butane-reservoir, and two or three times washed out with the vapour. Finally it was filled with vapour, while the reservoir was cooled to —8° C. At the temperature of the room the vapour is then so far removed from saturation, that irregularities owing to condensation in the capillary need not be feared.

Again the results may contain a small error owing to the uncertainty by the drop-method used.

$m=1.09$ grms.

x	1	2	3	4
t	46.6	52.5	59.3	68.9
temp.	14.7°.			

The deviations from the straight line were much smaller than in all the other determinations.

Calculation gives

$a=0.11$ $b=45.69$.

In steam

$m=1.09$ grms

x	1	2	3	4
t	60.4	67.7	76.5	86.5.

The deviations are again upwards and more pronounced than in the previous determination.

$a=0.11$. $b=59.40$.

Second observation at room-temperature.

$m=1.09$

x	1	2	3	4
t	47.0	53.4	60.8	68.3
temp.	16.0°.			

The deviations have increased and agree in magnitude with these in the other observations

$a=0.12$. $b=45.74$.

The differences in the two sets of measurements at room-temperature also point at accidental changes of the capillary action, possibly due to the formation or disappearance of a layer of vapour on the wall of the tube.

The relative viscosity follows from the equation

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \left\{ 1 + \frac{4\, G_2}{R} \left(\frac{G_1}{G_2} - 1 \right) \right\},$$

where the indices 1 and 2 refer to butane and air of 15.°5 respectively, while

$$\frac{G_1}{G_2} = \frac{\eta_1}{\eta_2} \sqrt{\frac{p_2 d_2}{p_1 d_1}} \text{ and } \frac{4\, G_2}{R} = \frac{.00001}{.02} = .0005.$$

These equations give for the viscosity of butane vapour relatively to that of air at 15.5°

at 14.7°	$\frac{\eta_1}{\eta_2} = .4661.$
at 16.0°	.4666.
at 100°	.6059.

The viscosity of air at 15.°5 is given by RANKINE equal to .0001803. The viscosity of normal butane thus becomes

temp.	14.7°	η .00008404
	16.0°	08413
	100°	1092

Of the other saturated hydrocarbons the only ones that we found mentioned are

methane temp.	0°	.0001040	GRAHAM [1])
	20°	1201	
isopentane	100°	08851	RAPPENECKER [2])
	212.5°	1164	

SUTHERLAND'S formula which gives a connection between the temperature and the viscosity of the vapour is

$$\eta_1 = \eta_0 \frac{T_0 + C}{T_0^{3/2}} \frac{T_1^{3/2}}{T_1 + C}.$$

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[1]) GRAHAM, Phil. Trans. Lond. III, p. 573; 1864.

[2]) RAPPENECKER, ZS. Physik. Ch. 72, 695; 1910.

For isopentane RAPPENECKER deduces from his observations $C=500$; for normal butane we find from the above data $C=349$. GRAHAM'S data for methane give a negative C.

Isopentane at 100.0° C corresponds with normal butane at 70.0° (reduced temperature $t=.809$.) SUTHERLAND'S formula gives for the viscosity of butane at this temperature .0001005. In order to compare the two results at $t=.809$ we have calculated for these vapours the constant $\eta^{-1} M^{1/2} T_k^{-1}{}_6 p_k^{2/3}$, which KAMERLINGH ONNES[1]) has given for liquids. For comparison we have added the values calculated for methyl chloride, benzene and nitrous oxide, with data taken from LANDOLT'S Tables (4th edition).

$t=.809$	C	$\eta . 10^7$	T	M	T_k	p_k	$M^{1/2} T_k^{-1/6} p_k^{2/3}$	$\eta^{-1} M^{1/2} T_k^{-1/6} p_k^{2}$
n. butane	349	1005	343.1°	58.08	423.9	37.5	31.15	310 × 10^3
isopentane	500	885.1	373.1°	72.10	460.9	32.9	31.57	354 × 10^3
methyl chloride	454	1082	366.6°	50.48	416.1	66.0	42.47	393 × 10^3
benzene	700	1249	455.0°	78.05	562.4	47.9	40.25	323 × 10^3
nitrous oxide	313	1342	249.6°	44.02	308.5	75.0	45.38	388 × 10^3

The agreement as regards the hydrocarbons is not so near as for the liquids. For the rest the numbers do not diverge more than for the liquids, the data for which are given below for comparison. In the computation we have used for butane [2]) our own determination, for the saturated hydrocarbons the data of THORPE and RODGER [3]), for the remaining substances the figures given by M. DE HAAS [4]).

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[1]) H. KAMERLINGH ONNES and W. H. KEESOM, Comm. Leiden Suppl. N⁰. 23, p. 85.

[2]) J. P. KUENEN and S. W. VISSER, Comm. Leiden, N⁰. 136.

[3]) THORPE and RODGER, Phil. Trans, 185A; 440; 1894.

[4]) M. DE HAAS, Comm. Leiden N⁰. 12, p. 12; 1894.

		$\eta \times 10^5$	$\eta^{-1} M^{1/2} T_k^{-1/6} p_k^{2/3}$
t = .60	n. butane	250	12460
„	n. pentane	270	11600
„	n. hexane	287	10950
„	n. heptane	301	10470
„	n. octane	322	9747
„	isopentane	263	11940
t = .58	benzene	420	9700
„	toluene	334	11720
„	methyl chloride	288	14790
„	butyl iodide	533	11250
„	ethyl ether	286	11720

COMMUNICATIONS

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BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 138^b.

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J. P. KUENEN and S. W. VISSER. The virial-coefficient B for normal butane.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **27 September 1913**, p. 330—335.)

EDUARD IJDO. — PRINTER — LEIDEN.

J: P. **KUENEN** and S. W. **VISSER**. *The virial-coefficient B for normal butane.*

Determinations of the vapour density of normal butane have enabled us to calculate the virial-coefficient B in the empirical equation of state as established by KAMERLINGH ONNES [1]). In the course of these calculations anomalies appeared which may be explained by the presence of a small quantity of a lighter admixture: a confirmation of this supposition was obtained by determinations of the boiling point and from the critical temperature.

The vapour density was determined by weighing. For this purpose a glass bulb of about .4 litre was used, provided with a stopcock and ground joint by means of which it could be connected to a butane-reservoir, a mercury pump and an open mercury manometer.

The volume of the bulb was determined by weighing with air First the weight of the bulb was determined after having been exhausted as completely as possible by the mercury pump. In all the weighings a tarra-bulb of about the same external volume was suspended from the other arm of the balance: the reading was not taken until the equilibrium had become constant.

The pressure of the air and afterwards of butane was first of all taken equal to the atmospheric pressure, the temperature being that of the room. For this purpose a tube some metres long with a stopcock was attached to the filling-apparatus. The gas was admitted to a pressure of about 1 m m. above the atmospheric: by opening the tap at the end of the long tube for a moment, the excess pressure could be let off without appreciable change of temperature and without fear of outside air penetrating into the bulb. Immediately after closing the bulb the temperature and pressure were read. The bulb was then weighed. In filling the bulb with butane vapour it was three times washed out with the vapour and exhausted.

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[1]) H. KAMERLINGH ONNES and W. H. KEESOM. Comm. Leiden, Suppl. N⁰. 23; § 36; p. 114, seq.

The barometric pressures were reduced to 0° and in the weights at temperatures above 0° a correction was applied for the expansion of the glass.

In the same manner a determination with butane was made at 0°, the bulb having been kept in ice for at least half an hour. During the operation the butane-reservoir was also placed in ice to prevent distillation of liquid into the bulb. After the weighing, the weight of the empty bulb was determined a second time as a test.

Subsequently determinations at room temperature were made at pressures of $^1/_2$ and $^1/_4$ atm The pressure was in this case read on the mercury-gauge.

It appeared necessary to determine the contraction of the bulb by the diminution of the internal pressure. For this purpose the weight of air contained in the bulb at a pressure of $^1/_3$ of an atm. was measured.

Finally two weighings were made with butane-vapour at 0° and at $^1/_3$ and $^2/_3$ of an atm.

MEASUREMENTS [1]).

Empty bulb. The tarra-bulb + 8 grammes made equilibrium with the empty bulb + .84036 gr. A later weighing gave .84033, a third .84036. The mean of these is .84035. This weight is in error by an amount x, owing to the change of the external volume by exhaustion.

Bulb with dry air. At 18.58° and 76.738 cms. the weight of the air was found to be .47370 grms; a second weighing gave .47735 grms. at 16 88° and 76.805 cms. For the weight at 0° and 76 cms. they give .5009 grms and .5014 grms, the mean of which is .5012 grms. This figure has to be increased by the amount x mentioned above.

Bulb with dry air at lower internal pressure. At a pressure of 26.816 cms and a temperature of 16.17° the air weighed .16596 grms. The weight of the air contained in the bulb at 0° and 76 cms would have been .49899 grms. It is easily proved, that the error of this figure owing to the change of external volume is approximately equal to x. The difference between .5012 and .49899 is therefore independent of x and represents the diminution of weight due to the diminution of internal volume at the lower pressure: as the diminution may be taken proportional to the change of pressure, it follows that the diminution of weight for 1 atmosphere would be .00333 grms. The external change of volume being approximately equal to the internal change, this latter weight is equal to the correction x. The weight at 0° and 1 atm. is thus $.5012 + .0033 = .5045$ grms From this weight the volume is found by dividing by the normal density of air. The measured weights of butane have also to be corrected by amounts proportional to x and to the pressure expressed as a fraction of 76 cms.

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[1]) The calculations as given here differ slightly from those in the dutch edition owing to a correction which had been overlooked.

Bulb with butane vapour.

The following table gives the results of the 6 weighings.

	Temp.	Pressure	Weight	Weight corrected.	Volume.
I.	16.63°	76.08 cm	0.98219 grms.	0.98513	390.1 cm.
II.	0.00	75.68	1.04400	1.04733	390.1
III.	21.02	40.42	0.50339	0.50469	388.9
IV.	19.94	18.57	0.22935	0.23016	388.1
V.	0.00	23.48	0.31244	0.31347	388.3
VI.	0.00	48.89	0.66184	0.66398	389.2

EMPIRICAL REDUCED EQUATION OF STATE.

The equation of state was taken in the form (Comm. Leiden, Suppl. 23):

$$pv = A\left(1+\frac{B}{v}+\frac{C}{v^2}+\frac{D}{v^4}+\frac{E}{v^6}+\frac{F}{v^8}\right) \quad . \quad . \quad . \quad (1)$$

where p is the pressure in atmospheres at 45° latitude, v the volume of 1 gramme expressed in the theoretical normal volume as unit, further:

$$A = RT;\ B = \frac{RT_k}{p_k}\mathfrak{B};\quad C = \frac{R^2 T_k{}^2}{p_k{}^2}\mathfrak{C},\ \text{etc.}$$

$\mathfrak{B}$, $\mathfrak{C}$, etc. represent the "reduced virial coefficients", quantities which depend on T only and must be equal for different substances, except for small individual deviations.

D and the subsequent coefficients may be neglected for pressures smaller than $^1/_7\ p_k$.

By introducing p as the independent variable instead of v equation (1) assumes the form:

$$pv = RT\left(1 + \frac{B}{RT}p + \frac{C - B^2}{R^2T^2}p^2\right) \quad . \quad . \quad . \quad . \quad (2)$$

The theoretical normal volume of pure butane is

$$22412 : 58\ 08 = 386.0$$

where 22412 is the normal volume of one gramme-molecule and 58.08 the molar weight of butane. When the constants were calculated on this basis, large deviations from the reduced equation of state were found. This finds a ready explanation in the fact, that the butane was not absolutely pure. It seemed therefore preferable to treat the theoretical normal volume as an unknown quantity and deduce it together with the other contants from the observations. It was for this purpose, that the above weighings at 0° at three different pressures were made.

Substituting in (2) p_5, v_5 and p_6, v_6 respectively and dividing the two resulting equations, we obtain the relation

$$1 - \frac{p_5v_5}{p_6v_6} = \frac{B}{RT}(p_6 - p_5) - \frac{B^2}{R^2T^2}(p_6 - p_5)\left\{p_6 + \left(1 - \frac{C}{B^2}\right)(p_5 + p_6)\right\} \ .$$

In this equation we may take for v_5 and v_6 the volumes of 1 gramme in ccm. The term containing C is of minor inportance: C may therefore be calculated with sufficient accuracy from the reduced coefficient $\mathfrak{C}$, which is known from measurements on a number of other substances.

From equation (3) was found $B = -.0430$.

In the same manner the second and sixth weighings gave $B = -\ .0431$; as the mean was taken .0431.

The theoretical normal volume of the butane used may now be calculated from equation (2): it becomes 387.9.

The difference of this figure from the value for pure butane (386.0) gives an indication as to the amount of the impurity: it points to the presence of a lighter admixture. The difference is less than .5%.

Using the normal volume found in this manner we may now deduce the virial coefficients B in the measurements at other temperatures.

t	B	B calculated.
0°	—.0431	—.0465
16.63	381	393
19.94	370	382
21.02	359	376

In the last column are given the values of B, as calculated from the mean reduced virial coefficient $\mathfrak{B}$ for a number of substances. The correspondence is satisfactory considered the degree of accuracy of the method by which B was here determined. An error in the fraction on the left side of equation (3) appears in B one hundred times enlarged; an error of 5 $^0/_0$ in B corresponds to an error of observation of $^1/_{2000}$.

Moreover a complete correspondence can in any case not be expected as the equation of state is after all only an approximation owing to the mutual deviations of the various substances with regard to the law of corresponding states. This is shown by the following table containing various values of $\mathfrak{B}$.

Reduced temperature .644.
mean reduced virial-coefficient $\mathfrak{B} = -1.12$.

	t	$\mathfrak{B}$
ammonia [1]	— 12° C.	— 1.22.
methyl chloride [1]	— 5	— 0.961
isopentane [2]	23.7	— 1.02
n. butane [3]	0.0	— 1.04.

Test of the impurity. The theoretical normal volume found 387.9 lead to a molar weight of 57.77. If we assume the admixture to be ethane, its amount may be calculated from the molar weights of ethane (30.05) and butane (58 08): the amount of ethane would appear to be 1 $^0/_0$.

The above result respecting the nature of the admixture finds confirmation in the boiling point of our butane. This point (— 1.0°)[4]

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[1] For these data we are indebted to Mr. G. HOLST whose results, which were worked out in the Leiden-Laboratory, will shortly be published as a thesis at Zürich.

[2] Calculated from S. YOUNG's data.

[3] Deduced from the above value of B.

[4] In Comm. N°. 125, p. 4 by a clerical error the boiling point was given as — 0.1°.

was derived from determinations of the vapour pressure in the neighbourhood of 0°.

temp.	press. (atm.)
12.0	1.6
0.00	1.049
0.00	1.046
—6.6	0.79

Owing to the presence of a more volatile admixture (ethane) the boiling point will be too low. In order to remove it to a certain extent the butane was cooled in solid carbon dioxide and vapour was pumped off. After this operation the vapour pressure at 0° was again measured; it was now 1.035 atm. The boiling point has therefore actually been raised : it now becomes —.8°. In repeating the same operation a large portion of the vapour coming off was collected in the bulb of the mercury pump. The pressure above the small quantity of liquid left, appeared to have diminished to 1.027 atm, which means a further rise of the boiling point: the final value may be taken at —.6° C.

A further confirmation of the presence of an admixture like ethane is afforded by the value of the critical temperature (150.8°). When for the various saturated hydrocarbons a graphical curve is drawn with the molar weights as abscissae and the corresponding critical temperatures as ordinates, the value found for butane seems to be a little too small. By representing the critical temperatures of ethane (305 3°), pentane (470.3°), hexane (507.9°), heptane (539.95°) and octane (569.3°) as an arithmetical series of the fourth order, we find for propane 370.25° instead of the experimental value 370.1° and for butane 424.94°, i.e. 1.04° higher than what was obtained by us. This result also points to a deviation of the critical temperature owing to the presence of a more volatile admixture.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 138^c.

⁂

C. A. CROMMELIN. Isothermals of monatomic substances and their binary mixtures. XV. The vapour pressure of solid and liquid argon, from the critical point down to — 206°.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **25 October 1913**, p. 510—519).

EDUARD IJDO — PRINTER — LEIDEN.

Errata Communication N⁰. 138*c*.

p. 23 line 6 from the bottom: for niterpolation read interpolation.

C. A. CROMMELIN. *Isothermals of monatomic substances and their binary mixtures. XV. The vapour pressure of solid and liquid argon, from the critical point down to* — 206°.

§ 1. In this paper the completed results are given of all the observations that I have so far made concerning the vapour pressure

TABLE I.

Date	N⁰.	θ (Celsius in Kelvin degrees).	p_{coex} in int atm.	p_{coex} in cm. merc.	
1910 14 Febr.	X	— 122.44	47.996	3645.1	critic. point
14 „	IX	— 122.49	47 890	3637.1	liquid—vapour
12 „	VIII	— 122.70	47.503	3607.7	
9 „	II	— 125.49	42.457	3224.5	
9 „	III and IV	— 129.83	35.846	2722.4	
10 „	V	— 134 72	29.264	2222.5	
10 „	VI	— 140.80	22 185	1684 9	
1912. 29 May	XI	— 150 57	13.707	1041.0	
24 „	XI*a*	— 161.23	7.4332	564.53	
16 Dec.	XII	— 183.01	1.3369	101.53	
16 „	XIII	— 184.25	1.1794	89.574	
16 „	XIV	— 185.42	1.0451	79 371	
16 „	XV	— 185.90	0.99379	75 475	
17 „	XVI	— 186.98	0.88575	67.270	
17 „	XVII	— 189 30	0.67896	51.565	triple point
18 „	XIX	— 191.36	0.51917	39 429	solid-vapour
18 „	XX	— 194 58	0.33051	25.101	
18 „	XXI	— 197.62	0.21526	16.348	
18 „	XXII	— 206.04	0.088443	6.717 1)	

For the boiling-point of argon under atmospheric pressure, by linear niterpolation between observations XIV and XV we find:

$$\theta = -185.84$$

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1) In repeating the measurements about the vapour pressures of solid argon, the experiments showed, that the figures of the lowest vapour pressure is incorrect. Improved determinations will be published before long. [Added in the translation].

of solid and liquid argon, besides some results which may be deduced from these observations.

The experimental material now at our disposal is put together in table I. (see p. 23).

The determinations in Febr. 1910 have already been published [1]), and are only included here to facilitate the complete survey of all the vapour pressure determinations, and because we shall need them in the following discussion of the results.

The observations in May 1912 were made on the occasion of the determinations of the straight diameter [2]); as regards the apparatus we can therefore refer to the papers concerning this. We need only remark that the pressure determinations were made with an open standard manometer [3]).

The measurements in Dec. 1912 were made with the apparatus already described [4]) for the determination of vapour pressure at low pressures, which on this occasion also proved highly satisfactory.

As regards this last series of measurements we make the following remarks. Before we proceeded to a measurement we waited until the constancy of the pressure showed that the equilibrium between the phases was established. During this period the temperature was of course kept as carefully as possible constant. The measurement then consisted in reading the manometer and barometer several times alternately. As a rule the pressure in the apparatus remained almost completely constant during a measurement.

The values given for the temperature of the bath of liquid oxygen, boiling under atmospheric and under reduced pressure, in which these measurements were made, were based upon a new comparison of the standard platinum resistance thermometer Pt_I with the hydrogen and the helium thermometers, shortly to be published by Kamerlingh Onnes and Holst. This gives results that differ slightly from the former calibration [5]) but for none of the temperatures are they more than 0°.05 and they are of a completely systematic character. The cause of this difference is not yet clear. A direct determination of the difference between the boiling point of argon and of oxygen will throw more light upon it.

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[1]) C. A. Crommelin, Comm. No. 115, and Thesis Leiden, 1910.

[2]) E. Mathias, H. Kamerlingh Onnes and C. A. Crommelin, Comm. No. 131*a*.

[3]) H. Kamerlingh Onnes, Comm. No. 44.

[4]) H Kamerlingh Onnes and C. Braak, Comm. No. 107*a*.

[5]) H. Kamerlingh Onnes and J. Clay, Comm. No. 95*c* and H. Kamerlingh Onnes, C. Braak and J. Clay, Comm. No. 101*a*.

My thanks are due to Mr. G HOLST, assistant at the Physical Laboratory, for making these temperature determinations, and for the calculations of the temperatures.

The determination of the triple point was made difficult by the undercooling phenomena which constantly appeared. If, while the temperature was just above the triple point, the temperature was slowly allowed to fall, it repeatedly happened that the whole mass of liquid argon crystallized out. By allowing the temperature to rise and fall with extreme slowness, and waiting patiently for the establishment of the equilibrium, I at last succeeded in establishing a temperature at which the three phases remained in equilibrium with each other for nearly two hours. During this period, the triple point was determined with an admirably constant pressure and temperature. This also gave me an opportunity of observing that the piece of solid argon sank in the liquid, and remained lying at the bottom of the tube, so that *in the triple point the density of solid argon is greater than that of liquid argon.* We shall presently be able to make use of this observation, although I had no opportunity to make a quantitative determination of the density of solid argon. Concerning the calculation of the observations, there is nothing particular to remark. An atmosphere in Leiden is reckoned at 75.9488 cm. mercury.

§ 2. Representation of the observations by formulae.

In order to get an useful representation of the observations by a formula, I first made use of RANKINE and BOSE's formula

$$\log p_{\text{coex}} = a_{\text{RB}} + b_{\text{RB}}\, T^{-1} + c_{\text{RB}}\, T^{-2} + d_{\text{RB}}\, T^{-3}$$

for the field of liquid-vapour as well as for that of solid-vapour. The result of the testing of the values of the pressure calculated from these formulae by the values observed, are found in table II.

As can be seen in the table, the correspondence is fairly satisfactory, especially in the part liquid-vapour, while it might be further improved for instance by the application of the method of least squares.

In the second place I have tried to apply to my observations

TABLE II.

Liquid-vapour.

$a_{RB} = +4.85033$. $b_{RB} = -634.391$. $c_{RB} = +30769.09$. $d_{RB} = -1076464$

θ	$p_{coex.}(O)$	$p_{coex.}(C)$	$O-C$ abs.	$O-C$ in %
— 122.44	47.996	47.886	+ 0.110	+ 0.23
122.49	47.890	47.797	+ 0.093	+ 0.19
122.70	47.503	47.422	+ 0.081	+ 0.17
125.49	42 457	42.646	— 0.189	— 0.45
129.83	35.846	35.908	— 0 062	— 0.17
134.72	29.264	29.264	0,000	0.00
140.80	22.185	22.289	— 0.104	— 0.47
150 57	13.707	13.707	0.000	0.00
161.23	7.4332	7.3961	+ 0.0371	+ 0.50
183.01	1.3369	1.3397	— 0.0028	— 0.21
184.25	1 1794	1.1825	— 0.0031	— 0.26
185 42	1 0451	1.0470	— 0.0019	— 0.18
185 90	0.99379	0.99492	— 0.00113	— 0.11
186.98	0.88575	0.88473	+ 0.00102	+ 0.12
189.30	0.67896	0.67896	0.00000	0 00

Solid-vapour. ¹)

$a_{RB} = +8.48993$. $b_{RB} = -849.4767$. $c_{RB} = -4204.71$. $d_{RB} = +122.3163$

θ	$p_{coex.}(O)$	$p_{coex.}(C)$	$O-C$ abs.	$O-C$ in %
— 189.30	0.67896	0.68126	— 0.00230	— 0.34
191.36	0.51917	0.51105	+ 0.00812	+ 1.56
194.58	0.33051	0.32861	+ 0,00190	+ 0.58
197.62	0 21526	0.22016	— 0,00490	— 2.28
206.04	0.088443	0.088028	+ 0.000415	+ 0.45

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¹) See note on p. 23.

NERNST'S [1]) vapour pressure formula. We may regard it as a purely empirical formula with 4 coefficients, written in the form

$$\text{lop}\ p_{\text{coex}} = \frac{A}{T} + BT + D \log T + C$$

and then calculate the coefficients which correspond best to the observations, without troubling about the theoretical significance of the coefficients. The result of a calculation of this kind is found in table III. The correspondence is considerably better than with RANKINE and BOSE's formula.

In the field of liquid-vapour the correspondence is less good, so that we have omitted the calculation of the results.

For practical use in the field of liquid-vapour therefore in our case, RANKINE-BOSE's formula is preferable to NERNST's At the same time the following calculation will show that NERNST's formula also in the field of liquid-vapour is capable of representing the observations as far as the critical point in a fairly satisfactory way, and in many cases, where the accuracy required is not so very great, may be a convenient help in calculation. I wrote the formula in the more usual form

TABLE III. Solid—vapour. [2])

$A = +9034.32.$ $B = -1.42112.$ $C = -1014.0278.$
$D + = 533.0275.$

θ	$p\,(O)$	$p\,(C)$	$O - C$ in $^0/_0$
− 189.30	0.67896	0.67764	+ 0.19
191.36	0.51917	0.51809	+ 0.21
194.58	0.33051	0.33197	− 0.45
197.62	0.21526	0.21526	0.00
206.04	0 088443	0.087942	+ 0.57

$$\log p_{\text{coex}} = -\frac{\lambda}{4.571\,.\,T} + 1.75 \log T - \frac{\varepsilon}{4.571}\,T + C$$

---

[1]) W. NERNST, Göttinger Nachr. 1906, p. 1.

[2]) See note on p. 23.

and took for the chemical contstant C in accordance with SACKUR[1]) the value 0.35, so that there now only remain two constants that are to be determined by the observations. With the value of the constants

$$\lambda = +\,1385 \text{ and } \varepsilon = +\,0.01446$$

we get a fairly good correspondence from the critical point down to the triplepoint, in which the deviations in p are all less than 2°/₀.

Finally I have tried to calculate all the terms of the formula, which SACKUR deduces from the heat theorem of NERNST, from the available calorimetric data, as SACKUR has done for some vapour pressure determinations by RAMSAY and TRAVERS[2]).

SACKUR writes the vapour pressure formula in the following form

$$\log p_{\text{coex}} = -\frac{\lambda}{2.3\,R\,T} + \frac{c_p}{R}\log T - \frac{1}{2.3}\int_0^T \frac{c}{T}\,dT + C + \frac{c_p}{2.3\,R} \quad {}^{3)}$$

in which λ means the heat of evaporation at the themperature T, c the specific heat of liquid or solid, c_p the specific heat of the vapour and R the gas constant (all for a grammemolecule of the substance).

I have only made calculations from this formula for the field of solid-vapour. The reason for this will be seen presently.

The measurements of DITTENBERGER[4]) and PIER[5]) both give the value of 4.91 for the molecular specific heat at constant pressure, of gaseous argon at higher temperatures. As in many cases it has been shown that this quantity is conspicuously independent of the temperature, we shall make use of it also for low temperatures.

For R we assume the value 1.985.

Concerning the value of c nothing is known experimentally. In order too arrive at a rational estimation, in spite of this, of the integral

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[1]) O. SACKUR, Ann. d. Physik (4) 40 (1913) p. 80.

[2]) W. RAMSAY and M. W. TRAVERS, Phil. Trans. (A) 197 (1901) pg. 47.

[3]) l. c. pg. 80.

[4]) W. DITTENRERGER, In. Diss. Halle 1897.

[5]) M. PIER, Zeitschr. f. Electrochemie 15 (1909) p. 536.

p. 29 line 7 from the top: for "which to two" read "which of the two".

p. 28 in the formula: for $\frac{1}{2.3} \int_0^T \frac{c}{T}\, dT$ read $\frac{1}{2\,3\,R} \int_0^T \frac{c}{T}\, dT$.

line 6 from the bottom: for too read to.

$\int_0^T \frac{c}{T}\,dT$ I calculated the frequency ν from LINDEMANN's [1]) formula

$$\nu = 2.80 \times 10^{12} \sqrt{\frac{T_0}{M v_0^{2/3}}}$$

(in which the index 0 refers to the melting point) and then values for c at the various temperatures by the formulae of NERNST-LINDEMANN [2]) and of DEBIJE [3]). In the field of temperature with which we have to deal, it makes no difference which to two formulae we use [4]).

Finally the values of the integral were determined by the graphic method.

Naturally these calculations could only be made for solid argon as NERNST-LINDEMANN's and DEBIJE's formulae only apply to solid substances.

If we take the value 1630 for the molecular heat of evaporation for all the temperatures in the field considered, a value which is chosen with a view to obtain the best correspondence, and which is not contrary to an extrapolation of the values of λ for the liquid given below then we find the following correspondence.

TABLE IV.

θ	$p\,(O)$	$p\,(C)$	$O-C$ in % of O
— 189.30	0 6790	0.6433	+ 5.3
191 36	0.5192	0.5050	+ 2.7
194.58	0.3305	0.3385	— 2.4
197.62	0.2153	0.2351	— 9.2
206.04	0.0884	0.0617	+ 30.0 [5])

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[1]) F. A. LINDEMANN, Physik. Zeitschr. 11 (1910) pg. 609 and W. NERNST and F. A. LINDEMANN, Berl. Sitz. Ber. 1911, pg. 494.

[2]) l. c.

[3]) P. DEBIJE, Ann. der Physik. (4) 39 (1912) pg. 789.

[4]) Tables for the calculation of c are published: for the formula of NERNST-LINDEMANN by F POLLITZER, Die Berechnung chemischer Affinitäten nach dem NERNST'schen Wärmetheorem, Enke. Stuttgart, pg. 162 sqq; for the formula of DEBIJE by W. NERNST. Berl. Sitz. Ber. 1912 pg. 1172.

[5]) See note on p. 23.

The correspondence obtained in this way, may be considered on the whole satisfactory.

I have to thank Mr. W. H. Keesom for many usefull suggestions in connection with these calculations.

§ 3. The triple point.

The triple point constants as observed are given in Table I. Calculation showed that the break of the two curves in argon is in the usual direction. In order to determine the values of $\left(\frac{dp}{dT}\right)_{\text{coex. vap. liq.}}$ and $\left(\frac{dp}{dT}\right)_{\text{coex. vap. sol.}}$ at the triple point as sharply as possible, I calculated for the triple point and for the two points lying immediately above and below it, the constants in the formula of Wrede-Rankine-Keesom $\log p_{\text{coex.}} = a_{\text{RK}} + b_{\text{RK}}\, T^{-1} + c_{\text{RK}}\, T^{-2}$ and by differentiation of this formula, the values of the differential coefficients.

In this way I found

$$\left(\frac{dp}{dT}\right)_{\text{coex. vap. liq.}} = 0.08162\,; \quad \left(\frac{dp}{dT}\right)_{\text{coex. vap. sol.}} = 0.08623.$$

As may be seen from these values there is a break in the usual direction although very slight.

From the observation already mentioned, that in the triple point the density of solid argon is greater than that of liquid argon, we may conclude, upon the ground of the general thermodynamical rules [1], about the triple point, that the melting curve from the triple point and in the immediate neighbourhood of it will run in the direction of the higher temperatures and pressures.

§ 4. Calculation of the heat of evaporation at different temperatures.

As the density of the liquid and of the saturated vapour is known along by far the greater part of the vapour pressure curve [2], we were able to calculate the heat of evaporation for p 31 line 4 from the bottom: for III read V.

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[1] Cf. H. W. Bakhuis Roozeboom, Die heterogenen Gleichgewichte, erstes Heft, pag. 94.

[2] E. Mathias, H. Kamerlingh Onnes and C. A. Crommelin, l. c.

a number of temperatures by the well known equation of Clapeyron-Clausius:

$$\lambda_{\text{liq. vap.}} = T\left(\frac{dp}{dT}\right)_{\text{coex.}} (v_{\text{vap.}} - v_{\text{liq.}})$$

For the simplication of the calculations those temperatures were chosen at which the vapour pressure determinations were made. The derivation of the liquid and vapour densities to these temperatures was done by the aid of the formulae that Keesom 1) has given for the curve of these densities. They are

$$\rho_{\text{liq.}} = \rho_{\text{k}} \left\{ 1 + A\,(1-\text{t}) + B\,(1-\text{t})^{\lambda} \right\}$$
$$\rho_{\text{vap.}} = \rho_{\text{k}} \left\{ 1 + A\,(1-\text{t}) - B\,(1-\text{t})^{\lambda} \right\}.$$

With the constants

$$A = +\,0.744537\,;\ B = +\,1.76408\,;\ \lambda = 0.341571$$

and the critical density $\rho_{\text{kRd}} = 0.53078$ 2) they give a very satisfactory correspondence with the observations, except for the vapour densities at the lowest temperatures, where the percentual deviations become very large. As, however, at these temperatures the vapour densities can be calculated by the ordinary gaslaws, this gives no difficulty.

The values of $\left(\frac{dp}{dT}\right)_{\text{coex.}}$ were calculated by the formula of Rankine-Bose already mentioned.

All quantities were expressed in *C. G. S.* units, and then the whole expression for the heat of evaporation divided by the mechanical equivalent, in order to get the result in calories per degree The results are shown in table III.

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1) W. H. Keesom Comm. N°. 79. See also J. E. Verschaffelt, Comm. N°. 25 and 55.

2) E. Mathias, H. Kamerlingh Onnes and C. A. Crommelin, l. c.

TABLE V. Heat of evaporation of argon.

θ	$\rho_{\Gamma \mathrm{vap.}}$	$\rho_{\Gamma \mathrm{liq.}}$	$\lambda_{\mathrm{liq.vap.}}$ in cal.
— 125.49	0.28727	0.78303	12.916
— 129.83	0.21451	0.88342	17.821
— 134.72	0.16621	0.96258	21.014
— 140.80	0.12115	1.04134	24 105
— 150.57	0 06854	1.13680	29.672
— 161.23	0.03723	1 22414	33.005
— 183.06	0.00814	1.37338	35.001

In conclusion I offer my hearty thanks to Prof. KAMERLINGH ONNES for the interest which he has taken in my work.

Errata Communication N⁰. 139.

p. 3 line 6 from the top: for „Communcation" read „Communication".

p. 4 line 19 from the top: for „$\frac{\partial H}{dy}$" read „$\frac{\partial H}{\partial y}$".

p. 5 „ 1 „ „ bottom: „ „case" read „ease".

p. 30 „ 9 „ „ top: „ „*CDL*" „ „*CDE*".

p. 30 „ 9 „ „ „ omit „from".

p. 30 „ 10 „ „ „ „ „*CE*".

p. 32 „ 5 „ „ „ for „if" read „of".

p. 33 „ 4 „ „ bottom: in the denominator for „54.2" read „54,9".

p. 35 „ 11 „ „ top: for „Investigations" read „rearches".

p. 37 „ 2 „ „ „ „ „ „ „

p. 39 „ 9 „ „ „ „ „if" „ „of".

p. 40 „ 10 „ „ bottom: for „tanks" „ „thanks".

p. 45 „ 2 „ „ top: for „cabibration" read „calibration".

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 139^a.

H. KAMERLINGH ONNES and ALBERT PERRIER.
Magnetic researches. X. Apparatus for the general cryomagnetic investigation of substances of small susceptibility.

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EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and ALBERT PERRIER. *Magnetic researches. X. Apparatus for the general cryomagnetic investigation of substances of small susceptibility.*

(October 25, 1913).

§ 1. *Introduction.* This paper contains the full description of the apparatus used in the investigation of Communcation III (Comm. N^0. 122*a*, continued in IV, Comm. N^0. 124*a*) of this series (May 1911). Various circumstances have retarded the extensive description which was promised there instead of the rough sketch.

The construction of the apparatus to be described forms part of a more general scheme to gradually obtain the necessary appliances for the investigation of weak magnetisation at low temperature. In doing this we did not confine our attention to special measurements, but intended to enlarge with as many appliances as possible the almost completely unknown "technique'' of investigation in this field.

On the one hand the measurement of magnetic forces, on the other that of magnetic couples suggest themselves. The ballistic method (measurement of flux) is only applied in the study of ferromagnetism [1]).

The method of couples is specially suitable for crystals and for isotropic bodies, which by their shape are seemingly magnetically anisotropic (e. g. ellipsoids). The apparatus with which our first measurements on the susceptibility of liquid and solid oxygen were made (Comm. N^0. 116, April 1910) is based on this method [2])

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[1]) In some cases which we will not dwell upon here this method might be resorted to.

[2]) The apparatus used by WEISS and KAMERLINGH ONNES for the investigation of ferromagnetism at low temperature (Comm. N^0. 114) belongs to the same type.

In a modified form this piece of apparatus will, we hope, be soon utilized in the cryomagnetic investigation of crystals.

In measuring forces a non-homogeneous field is used. Two cases have to be distinguished here.

For an object of small dimensions (the volume of which is v and the volume-susceptibility K) placed in the plane of symmetry between the poles of a magnet the force in the direction of the middle of the interferrum is given by

$$F = vKH \frac{\partial H}{\partial y}$$

where H indicates the intensity of the field and y the coordinate at right angles to the field.

For an object in the shape of a rod of uniform section s, the axis of which is in the plane of symmetry of the poles and passes through the middle of the interferrum, the relation is

$$F = \frac{K}{2} s \left(H''^2 - H'^2\right)$$

if H'' and H' are the values of the field-strength at the ends of the rod. When dealing with bodies of small dimensions by the method of FARADAY, the spherical object is placed where $H \frac{\partial H}{dy}$, therefore the force is a maximum. This is the method of procedure specially used by CURIE in his classical researches.

The rod-method, though applied long ago for measuring the susceptibility of liquids by QUINCKE's method, was hardly used at all in investigations on solids until 1910, when PASCAL adopted it in his important series of magneto-chemical researches [1]).

This is certainly curious, as the principle of the method is very simple and direct, but even more so as the disposition itself offers important advantages over the other methods. If one end of the rod is placed in the middle of the interferrum and care is taken that the other end is as far removed from it as possible, H'' obtains a maximum value and H' remains a quantity which may be neglected or need only be taken into account as a correction.

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[1]) P. PASCAL, C. R. 150, p. 1054. 1910. The priority of this application belongs to GOUY. C.R. 109, p. 935 1889.

The susceptibility is thus given by a single field-strength which is much more easily determined than the product $H \frac{\partial H}{\partial y}$, which has to be derived from several values of H, not to mention the fact, that the measurement itself of H in the middle of the interferrum, where the field is most nearly uniform, can be carried out much more accurately than at the point where the field is least uniform.

An *absolute* measurement by this method can therefore lead to a much more trustworthy result. Moreover in using a rod a much higher *sensibility* can be obtained, on the one hand because a larger quantity of the substance can be utilized, on the other hand because the intensity of the field in the middle of the interferrum can be raised to a much higher value without any objection, which is not by any means the case in the other method. Finally, as the field near the middle of the interferrum can usually be made approximately homogeneous over a space of 1 cc., it is of no great importance at what point exactly within that space the end of the rod under investigation is placed, so that as regards this a rough adjustment will be sufficient; the exact opposite holds when it is desired to place a body at the place of maximum action.

There are cases, however, in which only the method of maximum attraction can be applied, e.g. when the susceptibility depends on the field or when the available quantity of the substance is limited (e.g. on account of its rarity).

On the ground of the above considerations we have made it our object to construct a piece of apparatus *which in the first place is suitable for measurements with objects in the shape of an elongated cylinder, which may further, without important change, be adapted to the study of small objects placed at the point of maximum-attraction and finally, in addition to being suitable for solids, may also be used for the investigation of liquids, either by enclosing them in the movable part of the apparatus or by surrounding it as a bath.*

The case with which our apparatus may be adapted to the various requirements has shown itself a great advantage in our experiments [1]).

§ 2. *General arrangement of the apparatus* (comp. figure and perspective drawing). The main part of the apparatus is a *carrier* movably suspended along the axis of an enclosure which has the shape of a body of revolution. This enclosure is closed airtight, seeing that it must be capable of being exhausted and that it must be possible to maintain throughout the apparatus any pressure below atmospheric. This requirement from the side of cryogenics has its influence on the choice of most other parts.

The carrier the motion of which is guided along the vertical, carries at its lower end the experimental object which is placed between the poles of an electro-magnet with horizontal axis. The magnetic attraction or repulsion acts along the vertical and is *measured* by compensating it by means of the electromagnetic attraction of two co-axial magnetic coils, one of which is attached to the carrier while the other one is fixed. The force between the two coils is given by $F = ci_m\, i_f$, where i_m and i_f represent the currents in the movable and fixed coils and c is a constant which is determined once for all by using known forces (weights) [2]).

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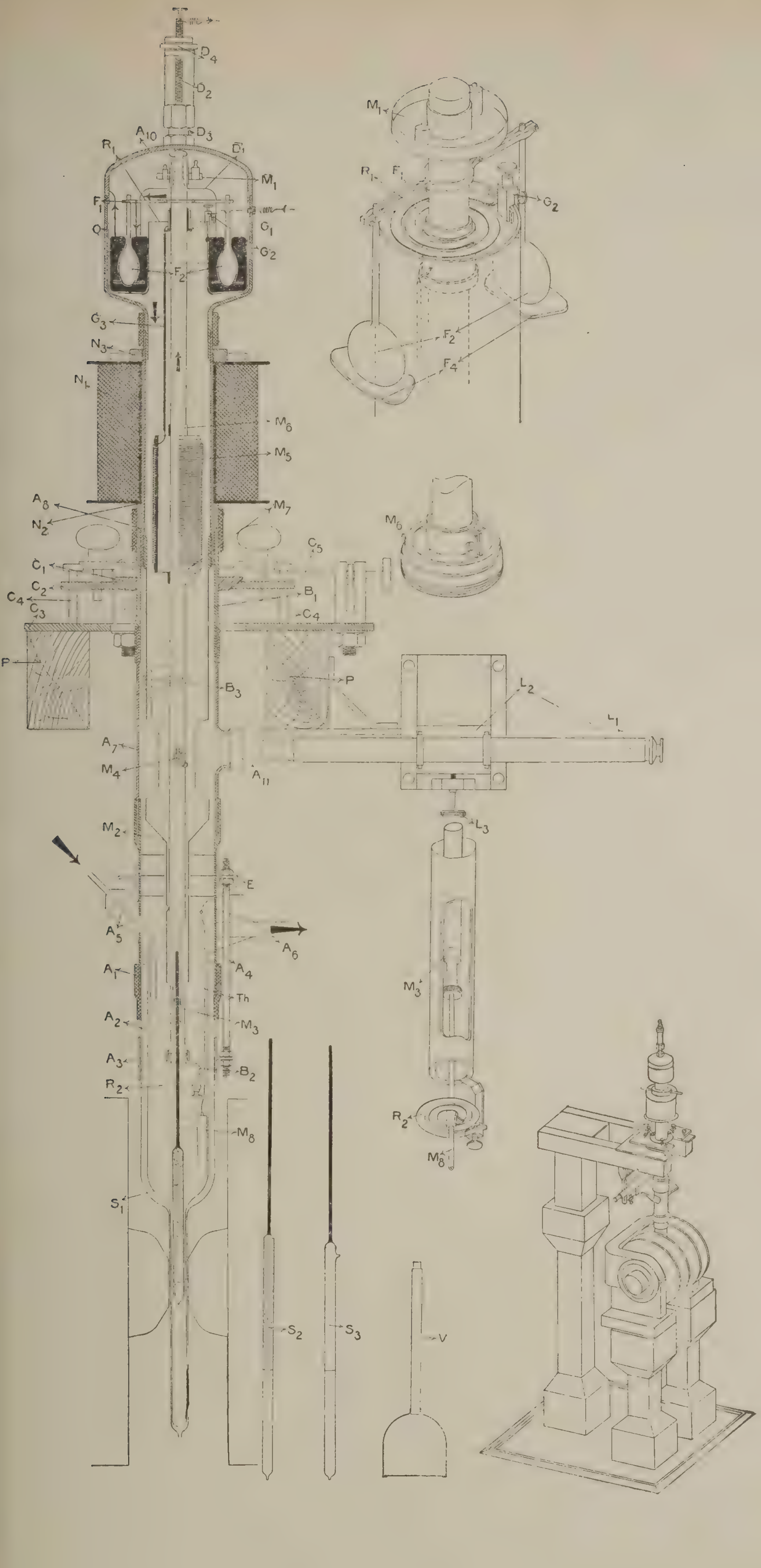
[1]) We may here recapitulate the various apparatus which in the mean time form the complete scheme planned by us:

depending on the use of couples	*a.* apparatus with ellipsoid (Comm. N^0. 116) *b.* ,, for crystals (to be constructed)
depending on the use of forces	*c.* hydrostatic apparatus (Comm. N^0. 116) *d.* apparatus for objects in the shape of spheres or cylinders (this Comm.)

a. has been used for liquid and solid oxygen, *c.* for liquid gases, *d.* for liquified or solidified gases and various solids.

[2]) For keeping in equilibrium an apparatus of the general type under consideration any kind of force may be used which can be changed gradually without touching the carrier. We can thus work equally well with a given compensating force (definite weights) and changing field (regulating the current through the electromagnet) as with a given field and changing electromagnetic compensating force. When our apparatus was first constructed we did not possess the necessary appliances for accurate field measurements, and in examining the dependence of the phenomena on the temperature we had to make ourselves independent of the change of the field by confining ourselves to the investigation of the magnetisation at different temperatures at a few field-stengths chosen beforehand and kept constant each time during the experiments.

For a modification in which the electromagnetic compensation is replaced by


D4
D2
D3
A10
R1
D1
M1
F1
Q
G1
G2
F2
G3
N3
N1
M6
M5
A8
N2
M7
C1
C5
C2
B1
C4
C3
C4
P
P
B3
L2
L1
A7
M4
A11
L3
M2
E
A5
A6
A1
A4
Th
M3
A2
M3
A3
B2
R2
R2
M8
M8
S1
S2
S3
V
M1
R1
F1
G2
F2
F4
M6

The electromagnetic compensation has for its sole object making a balance with the forces to be measured: the weight of the carrier itself is balanced *hydrostatically* by means of two floats immersed in mercury; the principle is therefore similar to that of a constant-volume hydrometer.

§ 3. *The various parts of the apparatus.*

a. The enclosure of the cryostat. The space inside the enclosure A of the apparatus is divided by screens E, which prevent exchange of heat between the two parts. The cryogenic part below the screens contains everything connected with the establishment of low temperatures, in the chamber above the screens which remains practically at constant temperature, all the delicate parts for the measurement of the forces are brought together.

The wall of the cryogenic space below E is of german silver. It is joined airtight by means of the india-rubber ring A_1 to the vacuum glass A_2 which contains the bath of liquid gas. The liquid gas is supplied by the german silver tube A_5, the vapours are carried off by A_6. The steel capillary of a heliumthermometer Th is soldered through the wall of the cap.

The upper part of the vacuum-glass is comparatively wide (6 cms), so that the liquid level falls very slowly during the evaporation, which as we shall see is of importance. By means of the copper ring A_3 and the rods A_4 the vacuumglass is firmly connected to the cap, that the considerable forces arising from changes of internal pressure may not change its position.

The part of the enclosure above the screens E is entirely of brass with the exception of tube A_7, which is glass.

At A_8 and at the joint with the upper part of the enclosure above N_3, A_9 (the letter is omitted in the figure), the parts fit each other with friction, which is of great convenience in the building up of the apparatus.

At the upper end the enclosure A is enlarged to a wide chamber

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a compensation by weights we refer to a forthcoming description of the apparatus which was usod in their investigations by KAMERLINGH ONNES and OOSTERHUIS (Comm. N⁰. 129*b* etc.).

containing the parts which serve to keep the carrier afloat. It is closed by an arched cover A_{10}, which again fits on the wall with friction. To this part of the enclosure is attached the german silver tube B_1 B_2 which narrows down towards the bottom and to which is fastened at B_2 the spring which guides the movable carrier in a vertical direction and the two stopping pins B_3, which prevent the carrier from moving too far up or down [1]).

The enclosure further serves to suspend the entire apparatus from two horizontal beams; by means of the ball socket C_1 C_2 the direction of the axis of the apparatus may be changed, without altering its height. The plate C_2 bears with three adjusting screws C_4 on the ground plate C_3, which in its turn is fixed to the beams, and may be shifted in a horizontal plane in two directions at right angles to each other by means of the screws C_5. With the adjusting screws the apparatus may be moved 3 cms up or down; this is necessary in using FARADAY's method in order to *find* the maximum force by displacing the apparatus with respect to the electromagnet.

b. The movable carrier with adjuncts. In the figure the carrier is indicated by M. It consists of a long thinwalled tube of brass, at the same time light and firm, lengthened by a narrow german silver tube which at its end carries a thread M_3. The experimental objects are also fitted with german silver top-pieces, which may be screwed on to M_3. They are thus easily attached to and detached from the carrier. At convenient heights the brass tube is provided with the following parts: the springs R_1 and R_2 which guide the motion, the marks M_4 for the purpose of reading the position of the carrier, a stopping ring B_8 for confining the motion between the pins, the electromagnetic coil M_5 moving with the carrier, the carriers F_1 of the floats and a scale M_1. As regards these various parts the following may be added.

c. Vertical guidance of the carrier. The space between the experimental objects and the inner wall of the vacuum-glass can sometimes not be more than a few tenths of a millimetre when measurements with strong fields are to be made; with the slightest movement of the axis of the carrier from its original position owing to a small asymmetry in the action of the electromagnet or any other cause the carrier would not be able to move up and down freely. This difficulty was quite satisfactorily overcome by guiding the carrier in its up and down motion by the aid of two flattened spiral springs [1]). The outer end of both is fastened to the stationary part of the apparatus, the inner end to the carrier and the plane of the springs is placed at right angles to the axis of the carrier. By the device of using flat springs a movement of the middle in the plane of each of the spirals is almost completely prevented. Usually the upper spring R_1 attached to the carrier remains the same, while each separate experimental object is provided with its own spring, which is removed from the apparatus with the object.

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[1]) The german silver tube might without disadvantage have been replaced by a simpler arrangement; in the design experiments were contemplated which were not carried out. If due care is taken, the stopping pins may also be dispensed with.

d. The hydrometric equilibrium. To keep the carrier afloat on mercury the upper chamber of the apparatus is provided with a ring-shaped trough Q (in our experiments of glass, later on of china) which is centred on the axis of the carrier. The latter is fitted with a horizontal arm F_1, in which at both ends are fixed the tubes of the floats F_2, glass bulbs, the shape of which is not unlike a flattened ellipsoid. The tubes of these bulbs which are of *very small section* are the only part that projects above the mercury. The section has to be small in order that the upward pressure of the mercury shall vary very little, if the apparatus is to be sensitive to a very small change of the vertical force acting on it. But the size cannot fall below a certain limit, because the tubes must also serve to compensate the diminution in upward pressure in the bath on the experimental object, owing to evaporation.

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[1]) Springs of that kind are made by cutting on the lathe a spiral groove 0.2 to 0.3 m.m. wide in a plate of german silver (comp. perspective figures R_1 R_2). By giving different widths to the spiral strip for a given diameter springs may be obtained of any desired degree of sensibility. The inner end is soldered to a small tube, the outer end is fixed in a clamping screw.

This compensation is effected by raising the level of the mercury. For this purpose use is made of a plunger D_1, a small glass flask of a shape corresponding to that of the trough which is moved up and down by means of a rod D_2 with thread and milled head D_4 passing through a stuffing box D_3. This contrivance, which was found very serviceable supplies the advantage that at the beginning the hydrostatic pressure of the bath need only be approximately compensated, which is done by placing a weight about equal to the pressure on the scale M_1; the accurate adjustment is made afterwards by regulating the level of the mercury.

e. The electromagnetic compensation. The fixed coil N_1 consists of 1275 turns of insulated copper wire, wound on a brass frame, sliding closely over the outside of the enclosure; the coil rests on the ring N_2 and is fixed at the top by the screw N_3. The movable coil M_5 has on the one hand to be as light as possible, on the other it has to produce as great a force as possible; account was therefore taken of the fact that for a given weight it is an advantage to make the radius of the coil large and the number of turns small. The coil contains 248 turns ($d = 0.7$ mm.) in two layers, wound on a thin-walled ebonite tube, which is held between two supporting brass rings $M_6 M_7$ in the shape of wheels, which may be clamped to the carrier at the desired height.

The wire which carries the current to the movable coil passes through and is insulated from the cover G_1 and is connected to the clamping screw G_2 of the upper spiral spring; the current passes through this spring to the ring by which it is attached and which is insulated with ebonite, along the wire G_3 to the coil and back through the carrier itself, the rod of the floats, a platinum wire dipping in the mercury, the mercury and finally a second platinum wire, which carries the current to the cover.

The electromagnetic system is calibrated once for all by fixing to the lower end instead of the experimental object a small scale, on which definite weights are placed, and regulating the current until the balance is obtained.

The level at which the carrier floats, is read on a glass plate M_4 with a scale division in tenths of a millimetre, which is focussed with a microscope L_1 magnifying about 40 times. For this purpose a window of thick plane-parallel glass is sealed on to an opening in the glass tube A_7. On the side opposite to the microscope behind the tube an electric glowlamp is placed in such a position that the scale divisions are seen light on a half-dark background: in this manner it may be very sharply determined when the cross fibre of the microscope exactly coincides with the division.

§ 4. *The experimental tubes.* The substances investigated by us (salts, powdered metal) are all enclosed in glass tubes, concerning which the following may be mentioned.

It is desirable, that the upward pressure due to the bath changes as little as possible when the liquid level falls through evaporation; for this reason the tubes end at the top in thin glass rods M_8 of 2 to 2.5 mm. diameter. The lower spiral spring R_2 and the thread by means of which the tube is screwed to the carrier are sealed to this rod with some KHOTINSKY glue. As regards the shape of the tube we have used different forms. Tubes as shown at S_1 are used for substances of high susceptibility, for which the magnetic action on the glass or on the bath plays a subordinate part, so that for them it may be entirely neglected or else a correction may be easily applied. The tube is filled with the substance, when it is still open, at the bottom putting in small quantities at the time, which are evenly compressed in order to obtain a tight filling and at the same time a uniform density throughout the whole tube; the substance is then closed in with a small plug of glass wool to prevent its being heated during the sealing of the tube and the tube is sealed off at the air-pump. The smaller the susceptibility of the substance the greater influence the susceptibility of the air would have and the more necessary it is to be assured of a good vacuum; a high vacuum, however, is obviously unnecessary.

In cases where account has to be taken of the susceptibility of the glass, which may give rise to fairly strong forces¹), tubes of type S_2 are used, the lower half of which, separated from the upper half by a glass partition, is exhausted. When this partition

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¹) The susceptibility of glass at low temperature was determined by us in Comm. N⁰. 124*a*, p. 6.

is placed on the level of the axis of the poles, the correction for the glass disappears, as it is divided symmetrically with respect to the axis; the susceptibility of the substance is in that case directly compared with that of the vacuum. Type S_3, which does not require further explanation is meant for the measurement of the susceptibility of the liquid in the bath.

§ 5. *Additional apparatus.* The electromagnet is a copy of WEISS's electromagnet which was used in previous researches of this series. The yoke is, however, placed horizontally this time, in order to leave the space below the apparatus completely free (comp. perspective drawing). Usually poles were used of the shape shown, the flat end-faces of which had a diameter of 40 mm. At a polar distance of 15 to 20 mms. the topographical inequality of the field about the middle of the interferrum was not above 0.1 $^0/_0$ within a distance of 1 cm The field-strengths were measured with a COTTON-balance of the usual pattern by W. G. WEBER of Zürich.

The circuits of the fixed and movable coils are entirely independent of each other: each of them contains an accurate ammeter, a commutator and rheostats, in which the current is reversed on commutation, in order to neutralise any magnetic influence on the ammeters. They are within reach of the observer seated in front of the microscope.

The field-strength of the electromagnet is given by the current flowing through it; the field was not adjusted until the magnetising current had been several times reversed.

If the evaporation of the bath in the apparatus as described is too strong, as is the case when liquid hydrogen is used, it is diminished by surrounding the bottom half of the vacuum-glass with a vacuum-glass with liquid air.

§ 6. *Method of observation.* Passing by certain simplifications which were often possible we proceeded as follows.

The enclosure and the carrier (without experimental tube) are first adjusted so that the common axis is vertical and passes through the centre of the interferrum. When this position is arrived at, the apparatus is not moved sideways any more.

The experimental tube is then screwed to the carrier and its spring clamped. By means of the weight on scale M_1 the carrier is made to float on the mercury approximately at the desired level and care is taken that the movable coil has the correct position relatively to the fixed coil. The apparatus as a whole is then moved in a vertical direction until the lower end of the experimental cylinder falls about in the line of the axis of the poles, after which the cylinder is adjusted more accurately by turning the apparatus about the ball socket C_1. When finally the poles have been brought at the right distance, everything is ready for the observations at ordinary temperature.

In changing to low temperatures as much weight is added to the scale as agrees approximately with the upward pressure of the bath to be expected and the cover is fastened to the apparatus air-tight by means of the india-rubber ring; after drawing out the poles, the vacuum-glass is placed carefully round the experimental tube, connected airtight and centred in a manner similar to that used in the apparatus of WEISS and KAMERLINGH ONNES. After having made sure that everything is airtight, the liquid gas is admitted to the vacuum-glass, the poles are brought back to their position, and the carrier is adjusted to its zero by means of the plunger; the currents in the large electromagnet i_e and in the fixed coil i_f are adjusted to suitable whole numbers and the current i_m (in the movable coil) regulated by a gradual change of the resistance until the carrier has come back to the zero. The current i_m is then noted down and the operations are repeated for the 4 possible combinations of the currents i_e, i_f and i_m. Before and after each observation the zero-position of the carrier is observed or again adjusted; when the change amounts to only a few tenths of a millimetre, there is no objection to do this, more simply than by means of the plunger, by shifting the microscope a little.

(January 31, 1914).

§ 7. *Sources of error. Sensibility. Accuracy. Disturbing magnetic influences.* The action of the magnet upon the carrier without the experimental tube appeared to be negligible, even when the lower end of the carrier was reduced to the temperature of liquid hydrogen. The action upon the coil of the carrier was also imperceptible even when a much stronger current $i_{,,,}$ was passed through this coil than was used in our experiments [1]). Moreover, even if it should be of any importance, it would be eliminated by the above indicated method of observation. The influence of the stationary coil upon the higher conducting spring is probably not negligible, but it cannot cause any errors, as neither in the calibration nor in the observations is anything changed in this spring.

It may also be mentioned that by the manner in which the conductors are arranged, in connection with the order in which readings are taken, any influence of the electro-magnet or the rheostats upon the ammeters or of these upon each other, are eliminated. These influences are moreover very small.

Capillary action. At first we were rather uneasy about the capillary action between the rods of the floats and the mercury surface, and between the carriers of the experimental tube and the surface of the liquid in the bath. The regular return of the carriers to the same zero, proved that no disturbances from these causes occurred in our experiments. We had always given great care to keeping the mercury surface as pure as possible.

Vibrations. Vibrations of the ground have a very injurious effect upon the observations, as they are reproduced in the apparatus greatly magnified, and are likely to cause troublesome swinging of the floating carrier. Vibrations in the microscope caused by the vibration of the ground, which troubled us at first, could be avoided by fixing the microscope more firmly.

The carrier is moved by every change of the forces that act upon it, which causes vertical oscillations of great amplitude. To damp these, glass wings are attached to the floats, so that after 2 or 3 swings they come to rest. Finally, the vapour bubbles that constantly rise in the bath, cause small vertical movements of the carrier, which are more marked, the greater the density of the liquid gas is. Against these vibrations the comparatively large inert mass — about 200 grams — of the carrier combined with the damping just mentioned, proved to be the best expedient.

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[1]) When the axis of the coil falls exactly in the plane of symmetry of the poles and goes through the middle of the interferrum this force is strictly zero.

The damping could as a matter of fact have been made much greater, without any difficulty. But it was better not to go any further, as it would have made the movements of the apparatus aperiodic, and a few swings were very useful to bring the influence of the capillary action upon the carriers each time to the same value.

Sources of error in the experimental objects themselves.

For the calculation of the specific magnetisation, we need to know the *mass per unit of length* of the substance with which the experimental tube is filled. The total mass which the tube contains can be ascertained as accurately as we wish, but the length over which it is spread in the tube, owing to the irregularity of the extremities cannot be determined more accurately than within 0.2 to 0.3 m.m.

Further, it is assumed in the calculation that it is evenly distributed over the whole tube, which cannot be strictly accurate, owing to slight differences in diameter and slight differences in the degree of closeness which is attained in filling to different heights, but this error is certainly small, and only influences the *absolute* value of the *calculated susceptibility;* if the same experimental tube is used in the same position at the various temperatures, this error has no effect upon the *relative* results, which are the principle object of our research.

The relative results may however become inaccurate, if between two experiments at different temperatures, some anisotropic grains, which together form an isotropic mass, each take a different direction, e. g. so that the line of greatest susceptibility in them approaches the direction of the lines of force, since the mean susceptibility of the group will thereby be changed. We can avoid this happening unnoticed, by taking the observations at low temperature between two observations at ordinary temperature. To answer the more general question in how far an apparent isotropy can be obtained with substances which are in reality anisotropic, by pressing them in a more or less finely granulated condition into tubes of 5 to 8 m.m., we can, without changing the conditions in any other respect, repeat the experiments after having brought the experimental tube into another direction relatively to the lines of force, by turning it on its axis. In doubtful cases we applied this method.

Numerical data: The coils described, can carry currents of 6 amp. (i_f) and 1.5 amp. (i_m) respectively, for a quarter of an hour; the force which they then exert upon each other is about 25 grams. In the given arrangement this may therefore be regarded as the limit of the force which can be measured with the apparatus. Under favourable circumstances (little vibration) a change of 0.001 gram in the force acting upon the carrier can be observed. Generally speaking, the para-magnetic substances examined caused attractions of a few grams, sometimes even more. The accuracy of the results is therefore more limited by the accuracy of the ammeters, than by that of the apparatus itself. With two of the ammeters, in each of which we constantly adjusted on one of the scale divisions, it was possible to bring the relative sensibility to within a thousandth. The third was almost equally accurate. In the relative measurements of the susceptibility calculated, we can thus rely in general upon an accuracy of 0.2 to 0.3 $^0/_0$. The absolute accuracy suffers somewhat from the fact that we are not certain of the homogeneity of the experimental object (see above); but it is principally limited by the accuracy of the determination of the magnetic field, the square of which occurs in the formula for the susceptibility, and not by that of the apparatus.

There is one more important factor to be considered, viz. the constancy of the temperature of the bath. Disturbances in this will have a different effect with different substances, as the change in the susceptibility with the temperature is very unequal for different substances, especially when we approach the absolute zero.

In our experiments in general we did not observe any disturbances from irregularity of temperature. Only in the case of gadolinium sulphate, the susceptibility of which changes most with the temperature (1 $^0/_0$ for 0.2 degrees at 20° K.) the measurements in different fields (at different moments therefore) did not agree so well with eachother as might have been expected if we only considered the accuracy of the magnetic determinations.

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N°. 139ᵇ.

E. OOSTERHUIS. Magnetic researches. XI. Modification in the cryomagnetic apparatus of KAMERLINGH ONNES and PERRIER.

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E. OOSTERHUIS. *Magnetic researches.* XI. *Modification in the cryomagnetic apparatus of* KAMERLINGH ONNES and PERRIER.

(Presented at the meeting of January 31, 1914.)

In the researches on paramagnetism at low temperatures, described in Nos. VI, VII and VIII of this series (Comm. Nos. 129*b*, 132*e*, 134*d*), an apparatus was used, in the main the same as that constructed by KAMERLINGH ONNES and PERRIER, of which a complete description is found in Comm. N⁰. 139*a*.

In one particular, however, a change was made in the apparatus. The apparatus so changed, which was briefly indicated in § 1 of Comm. N⁰. 129*b*, is here more fully described. The force acting upon the experimental substance in the tube, when it is placed in an inhomogeneous magnetic field, was measured in KAMERLINGH ONNES and PERRIER'S apparatus by electro-magnetic compensation. This can be replaced with advantage by a compensation by means of weights, opportunity for which is given by the scale Q placed upon the carrier [1].

The hook S serves to move the weights on and off the scale, while the apparatus remains air-tight; it can be moved from the outside, through the opening O. The rubber tube U is hermetically attached to the rim of the opening O, and also to the extremity of the hook; in this way, the tube and the hook together can be moved sufficiently [2]) to be able to lift the weights from the wall table W and place them on the scale, or vice versâ. The glass plate Z enables these manipulations to be watched from the outside. To prevent the rubber tube collapsing when there is a partial vacuum in the apparatus, it is supported on the inside by a flexible spiral of iron wire. We further refer to the figures, in which the upper portion of the apparatus, as it appears after our modification, is shown in section and seen from above. The lower part remained unchanged [1]).

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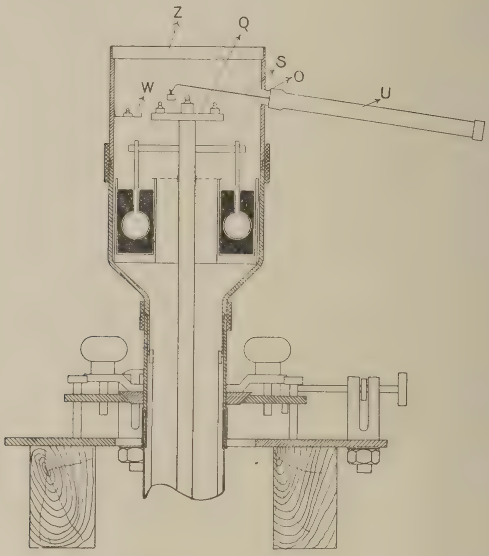
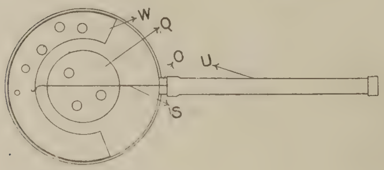
[1] In the apparatus described in Comm. N⁰. 139*a* there was also a scale fixed at the top of the carrier; the weights placed upon it did not however serve to measure the force, but only to obtain an approximate equilibrium against the upward pressure of the liquid. (See § 3*d* Comm. N⁰. 139*a*).

[2] Compare the similar arrangement for stirring in cryostats, Comm. N⁰. 83 § 4.





The arrangement here described has some advantages over that with the electro-magnetic compensation. In the first place, much greater forces can be measured by it, and moreover the method of working is simpler, as now only one current (that of the electro-magnet) has to be read, in the earlier arrangement three.

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[1]) The sectional drawing of the upper portion of the apparatus is drawn on the same scale as the fig. in Comm. N°. 139*a*, and gives therefore, if placed upon that, the complete drawing of the apparatus as used in the researches of Comm. Nos. 129*b*, 132*e* and 134*d*.

On the other hand, while in the former arrangement, the current through the electro-magnet was adjusted to certain fixed values, for which the corresponding strengths of field were accurately measured, in the modified arrangement it is best to place a certain weight upon the scale, and to regulate the current through the electro-magnet, until this weight is exactly compensated by the force exerted upon the experimental substance by the magnetic field. As the strength of field corresponding to this current must now be found by (graphic) interpolation, it can now only be as accurately known as by the method described in Comm. N^0. 139*a*, if the field has been determined for a great number of current strengths. Naturally in the method of compensation by weights we could also work with a few accurately measured magnetic fields, if we had a sufficient number of small weights at our disposal inside the apparatus; but working in this way would greatly decrease the simplicity of the method. For this reason in these investigations by the method of compensation with weights, the field for the Weiss electro-magnet for different strengths of current, was very minutely studied.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 139^{c}.

* * *

ALBERT PERRIER and H. KAMERLINGH ONNES.
Magnetic resarches. XII. The susceptibility of solid oxygen in two forms.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **28 Februari 1914**, p. 1004—1011.)

EDUARD IJDO — PRINTER — LEIDEN.

ALBERT PERRIER and H. KAMERLINGH ONNES. *Magnetic researches.* XII. *The susceptibility of solid oxygen in two forms.*

(Presented in the meeting of January 31, 1914.)

§ 1. *Introduction.* A former investigation [1]) had led us to the conclusion that the susceptibility of oxygen suddenly becomes considerably smaller when this substance changes into the solid state. How great the jump might be, was uncertain, owing to the absence of a bath which would keep the temperature constant at which this change takes place. We were therefore obliged to draw our conclusions from what we observed during a gradual heating, by which the temperature can be only imperfectly estimated. A further investigation was therefore necessary. Moreover, in repeating our determinations, we encountered the difficulty, that we found a different value for the susceptibility of solid oxygen at the temperature of liquid hydrogen, than in our first experiments, which were conducted according to a different method. Although we thought we were justified (Comm. N^0. 124) in considering that we had obtained reliable results only by the second method, and that in the meantime we need not attach any value to those obtained previously, it was still very desirable to confirm the more recent value for the jump by new measurements. Finally, in our experiments we came upon another problem that required to be solved. We had noticed (see Comm. N^0. 122*a*, May 1911), as WAHL [2]) also observed later, that solid oxygen, besides appearing in the blue-grey opaque form that it usually presents, also occurs in a transparent vitreous form. This modification can optically be very clearly distinguished from the liquid state. We conjectured that the transition from the transparent condition to the other one might be accompanied by a second jump in the magnetic condition, following on that which took place on freezing. We wished to ascertain the truth of this also.

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[1]) H. KAMERLINGH ONNES and ALBERT PERRIER. Leiden Comm. Nos. 116 and 124*a*.

[2]) Zeitschrift für physikal. Chemie. Bd. 84 (1913).

§ 2 *Arrangement of the experiments* For the magnetic determinations, as in previous investigations, we made use of the method of measuring the attraction which the magnetic field exerts upon a rod of the experimental substance placed at right angles to the field in the interferrum of an electro-magnet, and held suspended there by a carrier with hydrometer-arrangement.

More specially the arrangement of the apparatus was in the main the same as that used for our investigations of the liquid mixtures of oxygen and nitrogen, of which we shall give a complete description in the next paper (Comm. N^0. 139*d*). We do not give it here, because the investigation treated in this paper, is of a much more preliminary character than our investigation of mixtures, confining ourselves here in the main to that which is peculiar to our experiments on solid oxygen. At the outset it should be mentioned that the way in which the temporary connection was made between the carrier and the apparatus which introduced the oxygen from outside, was the same as in the experiments with mixtures of oxygen and nitrogen. In the further description we shall assume that the drawing of the apparatus as it is given in this paper will be consulted as a modification together with that of the next paper (N^0. 139*d*). The development of the apparatus there described, from our original apparatus and the modification due to OOSTERHUIS (Comm. N^0. 139*b*) will be obvious on comparison with Comm. N^0. 139*a*.

In the cryogenic part, we encountered in the first place a difficulty, which so far had not been provided for. Measurements had to be made at the temperatures between the melting-point of oxygen and the boiling-point of hydrogen, as well as at the temperatures of liquid and solid hydrogen. In order to be able to do this an arrangement was made which permitted us to work both in a bath of liquid hydrogen evaporating under various pressures, and in a bath of hydrogen gas, the temperature of which can be regulated.

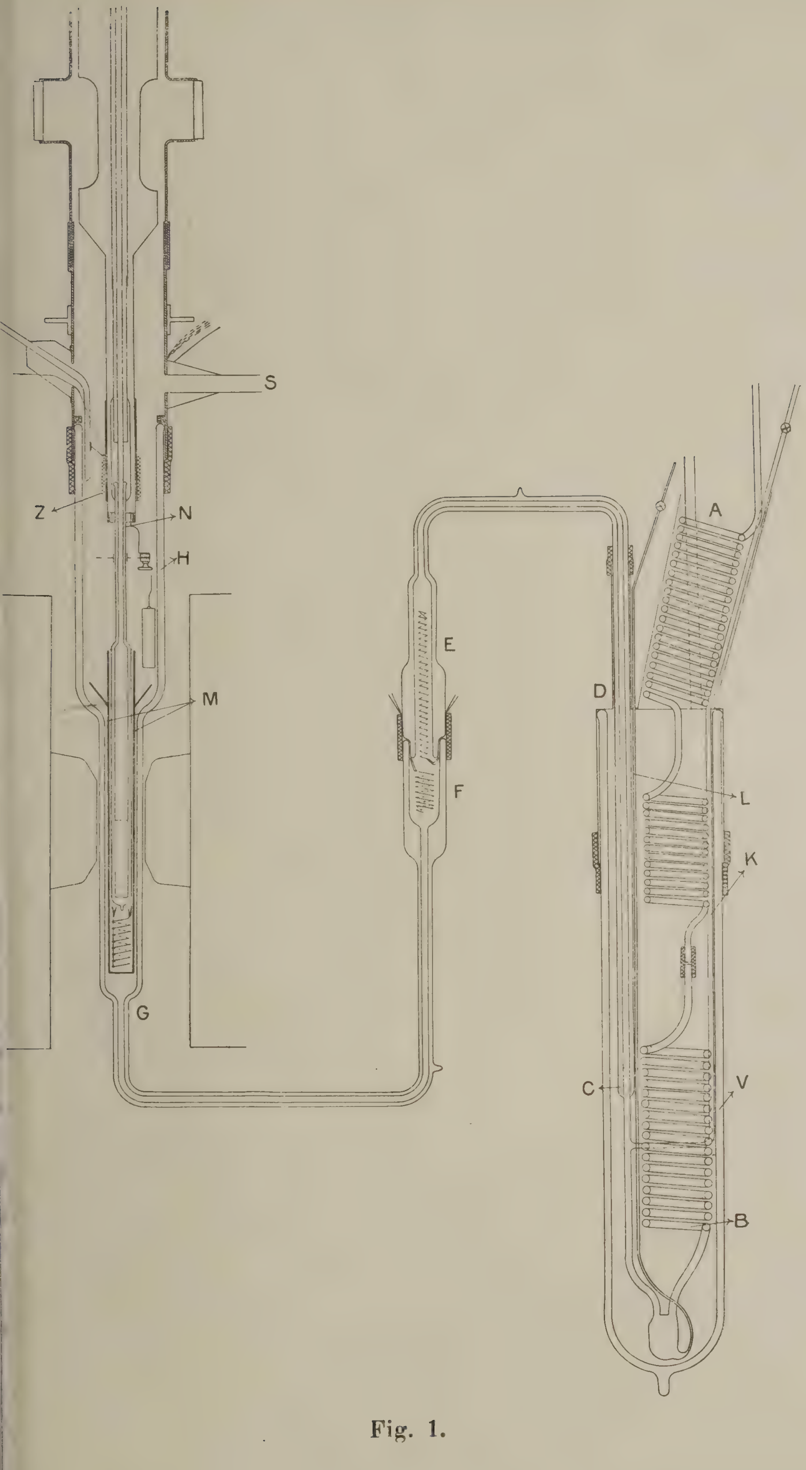

Fig. 1.

The arrangement consists principally in a circulation of hydrogen. The hydrogen after having been cooled to the boiling point, before it comes in contact with the experimental object, passes over a heating-spiral, in which JOULE heat is generated, and is thereby heated to the desired temperature. The whole hydrogen circulation is carefully shut off from the outside air. The gas streams from a supply-cylinder in which it is kept under pressure, through a copper spiral AB, the glass tube CDL, which from CE is double-walled, and silvered, and at E is widened, to the experimental space in the cryostat. It enters this through the twice bent double-walled tube FG, which forms the downward continuation of the vacuum-vessel of the cryostat. On the way down the gas is cooled by liquid air at A (copper spiral), and is further cooled first by hydrogen vapour and then by liquid hydrogen at B (glass spiral). At E the gas passes along a resistance thermometer; at F is the heating wire, at G in the lower part of the experimental space a resistance thermometer.

By means of regulating resistances the current through the heating wires is so regulated as to obtain the desired temperature in the experimental space. In the upper part of this there is a helium thermometer with a steel capillary, which forms part of our cryomagnetic apparatus in its usual form (Comm. N^0. 139a). The gas then rises further in the vacuum-vessel, and through S escapes into the gasometer or the air-pump. The tubes K and L serve for leading off hydrogen.

Of the various auxiliary apparatus we must further mention the thick-walled copper tube M, which surrounds the experimental tube, and which serves to keep the temperature of the gas which surrounds it even all over Of course liquid hydrogen can be introduced into the cryostat in the ordinary way, to immerse the experimental tube in a bath of liquid hydrogen.

We had a good deal of difficulty in procuring a rod of solid oxygen of about 5 or 6 cm. length, that was *completely filled*. As in freezing the volume of the oxygen diminishes by about $^1/_9$ there is a great tendency to form hollows. A homogeneous rod can only be obtained by allowing the liquid in the cylindrical mould to gradually freeze *from the bottom upwards*. As soon as solid matter settles in the neck of the tube, hollows must arise in the experimental mass, as the entrance of liquid oxygen is cut off [1]). The difficulty of procuring an homogeneous cylinder was increased by the fact that in our experiments the freezing had to take place inside a silvered vacuum glass, and could therefore not be followed by the eye.

In order to come a step nearer to the solution of this problem, which still presents difficulties, we made use of the possibility of regulating at pleasure the heat conducting power of a double-walled vacuum glass. The experimental tube in which the oxygen was frozen was made double-walled (not silvered); as much hydrogen was put in between the walls that the (small) pressure had exactly such a value, that according to preliminary experiments in a transparent bath the freezing took place under the most favourable circumstances. It appeared to be favourable to this that in the upper part of the tube latent heat was developed by the condensation of the gaseous oxygen which was admitted during the freezing. When a once formed stick partially melted, it was difficult to get it back into a dense condition. The double wall of the experimental tube is therefore also of use to eliminate temporary irregularities in the temperature of the surrounding bath (vapour or liquid). It was found that the temperature-range of the transparent modification did not extend more than 5 or 6 degrees below the melting point.

§ 3. *Results.* The figures in the following table are averages. To be able to express the results in absolute measure, the fields are measured in absolute measure, and the dimensions of the tubes carefully determined. The tubes were of the symmetrical type (see Comm. N⁰. 139*a* § 4), the lower part was evacuated, so that no correction was needed for the magnetism of the bath or of the wall. The oxygen used contained not more than 0.001 foreign admixtures. The immediate result of the observations is the susceptibility K per unit of volume; to calculate the value of χ, the specific susceptibility (or specific magnetisation coefficient), we must know the density ρ. We have taken 1.44 for this, on the ground of our determinations in 1910, and from a new one recently made, but neither determination can lay claim to great accuracy, so that the values if χ (and also of K for the opaque modification if it should prove that in this innumerable little splits are present) will have to be recalculated when ρ is better known.

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[1]) We shall return later to the freezing of oxygen and the change from the transparent to the opaque mass. When the access of gaseous oxygen is cut off, a long shaped hollow usually forms which as it increases assumes the shape of a worm fantastically coiled up in a confined space.

The four results refer to one freezing.

TABLE I.

Susceptibility of solid oxygen.

bath	T	$K.\,10^6$	$\chi\,.\,10^6$ ($\rho = 1.44$)
H_2 vap.	43°	166.1	115.3
H_2 liq.	20.3	79.	54.9
	17.3	77.3	53.7
	13.9	76.7	53.3

A new freezing gave two values for K near 165.5. 10^{-6} (before and after partial melting) at about the same temperature (—230° C). This value is less to be relied upon than that in the Table. We had very little time at our disposal for our joint work, and this was even diminished by the apparatus being found somewhat deficient in some points. On this account we had not time to test a temperature lying between the melting point and the transition point from the transparent to the opaque modification. But we had already postponed the resumption of our researches after the departure of one of us from Leiden, for two years, and we shall not have an opportunity in the near future to continue our joint research. We therefore felt bound to publish what we had so far established.

This is, besides the numerical values of our table within the limits of accuracy given for it, that the transition from the transparent modification of oxygen to the opaque, which takes place at about —225° C, *is not accompanied by any conspicuous magnetic modification*, so that it probably does not involve any important change in molecular structure. Further, that in the whole range from the freezing point of oxygen down to about —240° C the susceptibility is markedly less than in the liquid state. In this region it changes little with the temperature, in fact increases slightly on cooling. This does not seem to agree with the much smaller value which the table gives for —253° C, but here a phenomenon intervenes which has not been observed before, viz. that at about —240° C, the *susceptibility suddenly falls to about half its value.* The exact value of the temperature must still be more accurately determined; it is also not settled whether the transition is actually discontinuous or is completed in a very small range of temperature (1 or 2 degrees). The susceptibility falls in this transition to about the values that are found in liquid hydrogen.

It will be seen that these last values agree with the values of 1911, within the limits of accuracy of the latter. The results of 1910 are thereby, as we expected, condemned, and the cause to which we attributed the descrepancy between these results and those of 1910, gains in probability at the same time.

As regards the change in the susceptibility below —252° C with the temperature, although it is slight, yet it allows no doubt that it is a decrease. The observations permit the comparison of the susceptibility at different temperatures at constant density without the intervention of any correction. We have here, therefore, a new example of a substance that follows Curie's law at a higher temperature, and on approaching the absolute zero completely deviates from it. As the ratio of the susceptibilities observed above and below the transformation point is

$$\lambda_1 = \frac{115.3}{54.2} = 2.10,$$

it becomes probable that the exact value of the jump is precisely 2. For above 20° K., the magnetisation must still increase distinctly.

For the ratio of the susceptibility of liquid oxygen and solid oxygen at −230° C we find

$$\lambda_2 = \frac{313.3}{115.3} = 2.72.$$

This value is less certain than that of λ_1, for it contains the uncertainty concerning the density of solid oxygen and that of the change of susceptibility between −220° C and −230° C

From our previous investigations we had inferred a sudden change in the susceptibility to a fifth or sixth part of its value between the liquid state and the solid state at hydrogen temperatures. It now appears that a sudden change of this amount really exists, but takes place in two parts, namely, once to $^1/_3$ at freezing, and subsequently, after the susceptibility has again increased a second time, to $^1/_2$ at the transformation point —240° C, after which the susceptibility further decreases. In the accompanying figure our results are put together.

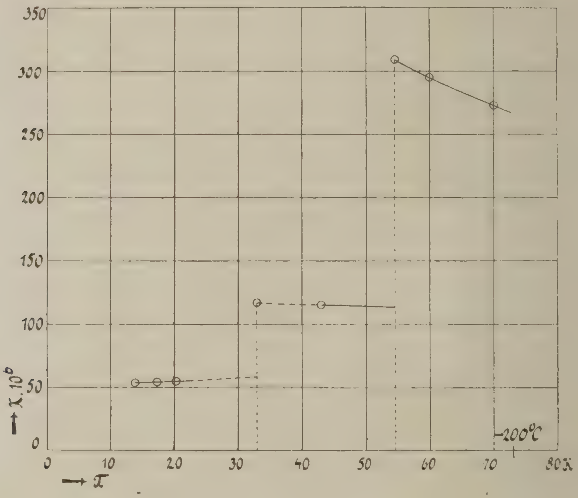

Fig. 2.

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ALBERT PERRIER and H. KAMERLINGH ONNES.
Magnetic Investigations. XIII. The susceptibility of liquid mixtures of oxygen and nitrogen, and the influence of the mutual distance of the molecules upon paramagnetism.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **28 Februari 1914**, p. 1012—1027).

EDUARD IJDO. — PRINTER — LEIDEN.

ALBERT PERRIER and H. KAMERLINGH ONNES. *Magnetic Investigations. XIII. The susceptibility of liquid mixtures of oxygen and nitrogen, and the influence of the mutual distance of the molecules upon paramagnetism.*

§ 1. *Introduction.* In 1910 and 1911 we published experiments upon the susceptibility of oxygen at very low temperatures, by which it was demonstrated that the specific susceptibility of this substance, which, in the gaseous form above 0° C follows CURIE-LANGEVIN's law, deviates considerably from this law, in the liquid state at low temperatures, and even more so in the solid state.

Subsequently we have observed similar phenomena in other substances (paramagnetic salts). The (solid) substances referred to follow CURIE's law at ordinary temperature, and also at temperatures that do not lie too far below it; but when the temperature falls to the neighbourhood of the boiling point or the freezing point of hydrogen, they deviate from the law *in various degrees*[1]*, but always in the direction of decrease of the susceptibility*

We think it advisable to recall here in a few words some of the views and hypotheses which guided us in the above-mentioned researches, in order to make clear the connection of the former experiments to eachother, and to the determinations we shall here deal with, and to elucidate the object of these last.

When we began our magnetic investigations at low temperature (in 1908) we wished, amongst other things, to test LANGEVIN's recently published theory of paramagnetism which leads to CURIE's law, at low temperatures.

On this account (and on others, see Comm. No. 116, § 1) it was natural we should begin with oxygen. The deviations that we found in oxygen together with what we observed in other substances, gave us ground to suppose phenomenologically that there would be a law of corresponding conditions for the deviations from Curie's law. This again gave rise to the question of how Langevin's theory would have to be supplemented in view of the new phenomena. Our first idea was the possibility of polymerisation, which might take the form of association in oxygen. As the degree of association of liquid oxygen if diluted with a non-active substance, would be changed, and as diamagnetic nitrogen could serve as such a substance, we thought (see Comm. No. 116 § 5) that by experiments on mixtures with this substance we should be able to ascertain whether it was a case of polymerisation or not.

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[1] KAMERLINGH ONNES and PERRIER, Comm. Nos. 116, 122*a*, 126*a*.

An experiment made with a less satisfactory apparatus than that which we now use, gave an indecisive result, and even led us to a wrong conclusion, as it seemed to support our assumption of the same change with temperature in the specific susceptibility of oxygen independent of the distance that the molecules were separated from eachother. In other words it still appeared to us possible that the specific susceptibility of oxygen vapour at the boiling-point might be the same as that of liquid oxygen, and that therefore gaseous oxygen at this temperature would deviate from Curie's law to the same extent as liquid oxygen. Our intention soon to make further measurements on mixtures of oxygen and nitrogen, came to nothing, as one of us left Leiden. It was a considerable time before we were able to continue our experiments.

In the mean time, Kamerlingh Onnes and Oosterhuis's investigations again raised the idea that the distance of the molecules in a paramagnetic substance certainly has an influence upon the deviations from Curie's law. Their investigation of oxygen of more than 100 times the normal density (Comm. N⁰. 134*d*, April 1913) demonstrated more specially that the susceptibility for gaseous oxygen can be represented down to — 130° C. with Curie's constant which holds for the ordinary temperature, which indicated the possibility that this might still be the case at — 183° C. This gave fresh support to what they added at the end of their paper of Jan. 1913 (Comm. No. 132*e*), showing the desirability of experiments upon the question, whether the bringing of the molecules (or atoms) of a paramagnetic substance to a greater distance from eachother, influences in itself the deviations from CURIE's law, and pointing out the importance of the continuation of our experiments with liquid mixtures of oxygen and nitrogen [1]).

Before we could at last begin these experiments in 1913 the importance of them was increased by yet another circumstance. Besides the hypotheses considered in the above mentioned article, hypotheses if another kind arose [2]).

With the former hypotheses, we do not interfere with the law of equipartition, but assume either polymerisation, as in the above case, or a subsiduary potential energy, a "molecular" field, the magnitude of which is determined, not only by the field but also by the amount of one-sidedness of the direction of the molecular magnetic axes (WEISS and FOËX, KAMERLINGH ONNES and OOSTERHUIS) [3]). In the new type (OOSTERHUIS, KEESOM) on the other hand a distribution of energy is supposed, which is determined according to the quantum-theory.

In the extreme form of this type no other suppositions are introduced than those of the quantum-theory. There is naturally room for transitional forms between this extreme form and the other type of hypothesis. These are got by assuming polymerisations or a molecular field besides the quantum-theory.

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[1]) Recently, WEISS (C. R. Dec. 1913) in deducing the distance law for the molecular field in ferromagnetic substances (comp. § 4 if this Comm.) points out the importance of investigations of the same material at different densities. See also G. FOËX, Ach. d. Sc. phys. et nat. Genève (4) XXXV 1913.

[3]) As had been partly the case with the hypotheses of the first kind, so also those of the new kind were partly suggested by our former magnetic investigations.

[3]) The hypothesis, that the resultant magnetic moment of the molecule changes, can be introduced in two different ways. In the first place, by assuming polymerisation, as mentioned above. In the second place by supposing that the change takes place exclusively within the molecule itself. By continuous change of this sort of course every deviation from CURIE's law may be explained. In that case there can be no question of decision between the above mentioned types of theory. The supposition referred to seems less acceptable also for this reason that in the cases in which WEISS was led to assume a change in the molecular moment, this was always a discontinuous alteration (by changes in the number of magnetons) and one which took place in all the molecules at once, while for the rest the moment within a definite temperature zone did not undergo any changes.

It is now of importance, not only for magnetism, but also for the law of molecular activity in general, to decide between these two different types of hypothesis, by experiment. The most important for this purpose are experiments in which the paramagnetic molecules are brought to different distances from eachother. For if the above mentioned question should be answered in the negative and it should be proved that the susceptibility per molecule remained the same at whatever distance they are from eachother, then all hypotheses of the first sort (mutual influences) would of course fall to the ground. The measurements which should demonstrate this would be an experimentum crucis.

The determination of the susceptibility of liquid mixtures of oxygen and nitrogen claims the first place in experiments upon the influence of the distance of the molecules upon the deviations from CURIE's law. The liquid (paramagnetic) oxygen exercises no chemical influence whatever upon the liquid (diamagnetic) nitrogen; the two substances can be mixed in any proportions, so that the distance of the paramagnetic oxygen molecules can be increased at pleasure: the mixtures remain moreover liquid down to a very low temperature, which is of particular importance, if the theory of quanta is to be applied. Experiments with these mixtures promised therefore a more distinct and more immediate decision than those with crystals and solutions of chemical compounds in different degrees of dilution ¹). In the investigation now completed we have not been able to do more than make a first survey of the difficult territory.

We here offer our sincere tanks to Dr. OOSTERHUIS, who has contributed greatly to the success of our work, by very carefully measuring out the field that served for our experiments, and by repeating certain susceptibility determinations which were doubtful.

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¹) With regard to these we may remark that the important investigations by CABRERA and MOLES (Arch. d. Genève (4) XXXV May 1913) of solutions of iron salts are of a chemical nature and assume the validity of CURIE's law. Their object is therefore quite different to ours, in which the point is to investigate the influence of the distance of the molecules of a *chemical element* dissolved in another *element*, upon a function of the temperature.

His measurements enabled us to introduce important corrections in our results.

§ 2. *Method.* The measurements were made by the attraction method, with a vertical cylinder of the substance to be investigated. One of the extremities of the cylinder is placed in the middle of the interferrum of an electro-magnet. As in the apparatus previously constructed by us [1]) the cylinder was attached to a vertically running carrier, and the forces were measured by a zero-method; in this the modification introduced by OOSTERHUIS [2]) was made use of, viz. the current through the electro-magnet was regulated, and therefore the field adjusted, until there was equilibrium with marked weights.

While thus the magnetic part of the experiments is about the same as that of the previous ones, the arrangement of the actual experimental object demands a number of special apparatus and precautions. A homogeneous mixture must be prepared of known proportion, and in a proportion chosen at will, of two substances, which are gaseous at ordinary temperature, and which are condensed in the experimental tube.

In the first place a communication must be made through the closed outer cover of the cryomagnetic apparatus (see description loc. cit.) with the apparatus for mixing and measuring the gases. For this purpose, the glass tube *A* (see fig. 1) which forms the central part of the carrier, is bent round three times rectangularly at *B*; further it bears a horizontal tap *C*, and terminates in a horizontal ground joint *D*, in which fits the ground extremity of the tube *E*, which protrudes outside. This tube is enclosed in a thick but elastic india-rubber covering, and can be pulled back about 2 centimetres, from outside, and made fast in this new position; in this way the connection with the carrier can be made; or it can be left *quite free*, without opening the cover. In the same way the tap *C* can be manipulated from the outside by means of a similar arrangement *F*.

The necessity of the mixture being homogeneous, entails

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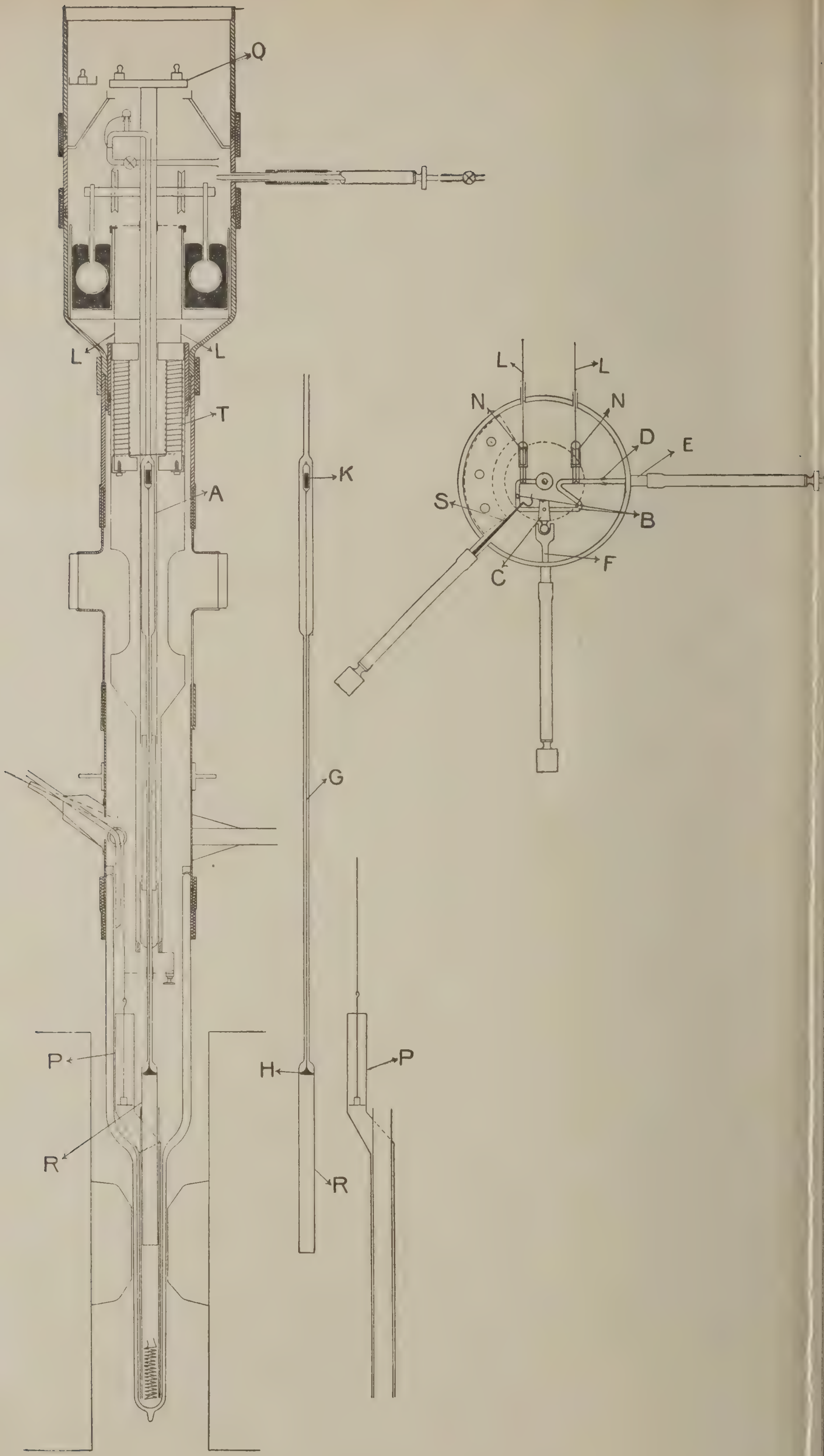
[1]) See H. KAMERLINGH ONNES and ALBERT PERRIER. Comm. No. 139*a*.

[2]) E. OOSTERHUIS. Comm. No. 139*b*.


Q
L
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S
B
C
F

vigorous stirring inside the experimental tube (the cylinder *R*, at the lower end of the carrier). Even when the mixture is homogeneous in the gaseous form, the oxygen which condenses more easily, will tend to collect at the bottom in the carrier; this difficulty is overcome by using a stirrer consisting of a very long thin glass capillary tube *G*, terminating in a small disk *H* (the actual stirrer), which carries a little piece of iron (*K*) at the top; the whole of which can be moved up and down through a distance equal to the height of the experimental tube. This movement is set in motion by the attraction of an electro-magnet *I* upon the piece of iron *K*; the electro-magnet is moved from outside the apparatus by means of two bronze strips *L*, which run over the pullies *N* and pass through the walls without friction, terminating in two elastic enclosures similar to *F* and *E*. These suspension-strips, which also serve as conductors for the electro-magnet, are moved by hand.

The carrier is provided at *B* with a small stopper serving as a safety valve, to guard against a casual excess of pressure in the carrier during the measurements, when the tap is closed, bursting the carrier.

The preparations for a series of measurements took place in the following order: when the enclosure is found to be air-tight, a sufficient weight is placed upon the plate *Q* to bring the carrier to its lowest position; the connection with the tube *E* can then be made, the tap *C* is then opened, and any gases that may be contained in the carrier, are pumped out. Then the cryogen bath (of pure liquid nitrogen) is made ready, and the temperature reduced to a few degrees below the boiling-point by reduction of the pressure. Finally the desired amount of pure oxygen, which has been previously measured in a volumenometer resembling a TÖPLER pump, can be condensed in the carrier, and then by means of the same instrument, the quantity of pure nitrogen required to completely fill the experimental tube *R*. After this *C* is shut, *D* is disconnected, the gas supply tube is pulled back and the overweight taken away; the carrier is then free, and completely closed against the vapour of the bath. While the bath is being brought to atmospheric pressure, and to an even temperature which is greatly helped by the pump-stirrer

P[1]) which causes a vertical circulation in the whole bath, the electro-magnet which serves as stirrer for the mixture, is put in motion, until the magnetic attraction, which is measured from time to time, reaches a constant value.

The question of what the composition of the mixture is deserves particular attention. A *given weight* of oxygen is introduced into the tube, which spreads over a given volume, known by the calibration of the experimental tube. The weight of oxygen per cm^3., i. e. the concentration, is thus given by immediate experiment, which quantity is also the most important from the magnetic point of view, as the measurements in the first place give the susceptibility of the mixture, and the concentration enables us to deduce from it the specific magnetism which can be ascribed to the oxygen alone. To compensate the vacuum caused by the contraction of the mixture by each decrease of temperature, we have each time added *pure nitrogen* (stirring of course each time); our object was the investigation of the influence of the mean *distance* of the paramagnetic molecules upon the magnetisation, and the process described above apparently comes to the determination of the changes in the magnetisation with the temperature, for every mixture at *constant distance* of the oxygen molecules.

After the measurements the vapour products were collected, and analysed with pyrogallic acid. This analysis is a useful check, but cannot lay claim to great accuracy, as the comparison with the synthesis assumes the knowledge of the total quantity of condensed nitrogen (including the amount added during the measurements) which quantity is for various reasons somewhat uncertain. Moreover it is necessary that the vapour products should be very completely collected, as a considerable weight attaches to what is vaporised last, as being almost pure oxygen. On the other hand we may remark that in the deduction of the concentration (see above) from the synthesis only an accurate knowledge of the *weight of oxygen* is assumed and not that of the nitrogen, and therefore can claim a greater degree of accuracy.

The susceptibilities are expressed in absolute units by comparison with that of pure liquid oxygen, which are previously measured

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1) See H. KAMERLINGH ONNES. Comm. No. 123, § 2.

in absolute value by the method of rise [1]); this cabibration comes simply to this, that a series of measurements are made under the same conditions as the former, but with pure oxygen instead of with the mixtures. Moreover, a calculation of the absolute values based upon the values of the field according to the measurements made by Dr. OOSTERHUIS in Leiden after the measurements, lead to results which agreed with the experiments previously obtained, well within the limits of experimental accuracy. Further the magnetic corrections were applied for the glass of the carrier and for the nitrogen of the bath as well as of the mixture [2]).

§ 3. *Conclusions and experimental results.* The mean numerical data of the measurements are given in table I, where χ signifies the magnetisation of 1 gram of oxygen in each of the mixtures or in the pure oxygen; for the latter the values are calculated on the basis of our measurements in 1910 (Comm. N⁰. 116); ρ is in each case the weight of oxygen per cM^3. (concentration), λ the approximate ratio between this weight and the corresponding one in the pure liquid; λ indicates to some extent the dilution (only approximately, because with the method followed λ changes with the temperature) [3]).

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[1]) KAMERLINGH ONNES and PERRIER. Comm. No. 116. Cf. note 1, pag. 15.

[2]) These corrections must be made even in a purely relative measurement, as they are by no means proportional to the susceptibility of the experimental object taken as a whole.

[3]) The various numerical data upon which the results are based are not all of the same degree of accuracy: the temperatures, measured by means of the pressure under which the liquid boils, the same pressures being chosen for the different mixtures, may be compared in the one and the other mixture to 0.1°, the absolute values, an the other hand, have the same degree of accuracy as the vapour pressure curves.

The directly found (volume) susceptibilities of the mixtures, which are not included in the table, may be compared with eachother to about 0 3 % on an average. As regards the *specific magnetisation coefficients*, if these may be compared *for the same mixture* at different temperatures with the same accuracy as the susceptibility, their uncertainty in *absolute value* is specially determined by that of the concentration; we estimate it on an average at 1.5 %, higher for the large concentrations, lower for the smaller ones.

Table I shows at once this qualitative result: *The specific magnetisation coefficient of oxygen becomes considerably greater, in proportion as the concentration diminishes, i. e. the additive rule is by no means followed in mixtures of oxygen and nitrogen.*

TABLE I.

Magnetisation-coefficients for oxygen. (77.°4 K. — 64.°2 K).

				(p = atm. pressure)		(p = 300 mm.)		(p = 100 mm.)	
		ρ		t	$\chi \cdot 10^6$	t	$\chi \cdot 10^6$	t	$\chi \cdot 10^6$
liquid oxygen pure		1.204		$-195^\circ.65$	259.6				
		1.235				$-202^\circ.2_3$	271.4		
		1.267						$-208^\circ.8_4$	284.9
Mixtures	I	0.745_8	$\frac{3}{5}$	$-195^\circ.65$	294.5	$-202^\circ.2_3$	314.5	-208.8_4	336.5
	II	0.401_0	$\frac{1}{3}$	.79	336.7	,,	359.6	,,	390.6
	III	0.230_4	$\frac{2}{11}$	.60	363 8	,,	393.0	,,	[423.5]
	IV	0.138_0	$\frac{1}{9}$	.65	383 6	$-202^\circ.2_3$	420.4	,,	459.8
	V	0.080_1	$\frac{1}{15}$	$-195^\circ\,80$	395.8	—	—	$-208\;8_4$	472.0
extrapolated by $\chi = \frac{0.03097}{T}$ (WEISS and PICCARD at 20° C.)				$-195^\circ.65$	400.0	$-202^\circ.2_3$	437.2	$-208^\circ.8_4$	482.2

From a somewhat more careful inspection, and the comparison with the last row of the table, it appears further that *with increasing dilution the magnetisation coefficient approaches to the values which satisfy the inverse proportionality with the absolute temperature*, starting from the number lately obtained by WEISS and PICCARD for gaseous oxygen (see also Fig. 3).

Without anticipating in any way the theoretical interpretations of these results, which will be treated in the next paragraph, we can phenomenologically express them as follows:

The deviations from Curie-Langevin's *law, shown by pure oxygen at low temperature, are not an immediate consequence of the change of temperature, but are caused by the increase of the density or by the distance between the molecules becoming smaller.*

Finally, let us examine more closely the *thermal change* for *each concentration*, by plotting $^1/_\chi$ as a function of T (Fig. 2). We see at once that the points obtained lie upon *parallel straight*

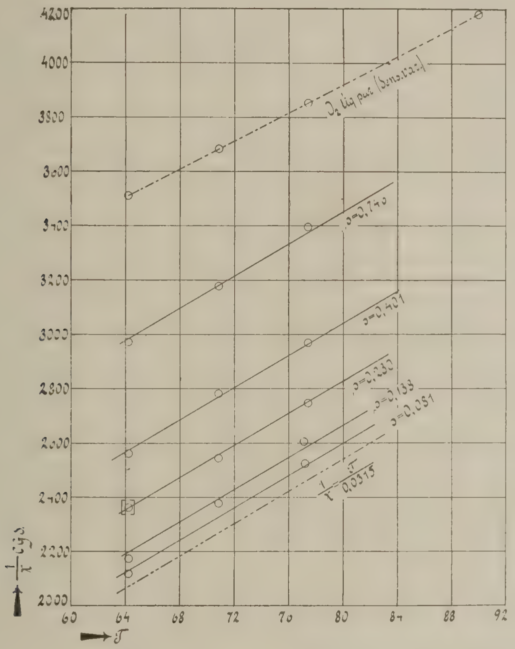

Fig. 2.

lines; the change with the temperature can therefore be represented [1]) within the limits of accuracy of the observations, by a relation of the form

$$\chi(T + \Delta) = const.,$$

in which only the parameter Δ changes from one concentration to the other. Table II shows this:

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[1]) As was found by Kamerlingh Onnes and Oosterhuis for liquid oxygen; Comm. No. 132*e*.

TABLE II.

Mixture	Δ	$\chi(T+\Delta)$		
		$T = 77.4_4$	$T = 70.8_6$	$T = 64.2_5$
I	29.5	0·0315	0.0316	0.0315
II	16.3	316	313	315
III	9.5	316	316	[312_5]
IV	4.5	314	316	316
V	2.2	316	—	314
Mean 0.0315_2				

Therefore: the *change in density of the oxygen only alters the specific magnetisation, without changing the* CURIE *constant.*

The pure liquid oxygen seems to form an exception: the straight line $^1/_\chi = f(T)$ for this differs considerably in direction from that for the mixtures. We would call attention to the fact, however, that each mixture was examined at constant concentration (see § 2); while this was not the case with pure oxygen, which shrinks considerably on cooling ($10\,^0/_0$ about between —183° and —210°); if we calculate for any temperature (say —195°) the specific magnetisation that pure oxygen would have at that temperature and at the densities corresponding to the other temperatures, using the CURIE constant which is common to the mixtures at constant concentration, the values obtained thus (see Fig. 3 the points indicated by black disks) fall in a natural way upon the general curve, which gives the specific magnetisation as a function of the concentration at the temperature under consideration; the data obtained from these measurements form therefore strong arguments in favour of the conclusion that in the investigation of *pure liquid oxygen at constant density a curve for the thermal change of the magnetisation would appear, which only differed from that for the mixtures by a new translation.* This causes the anomaly to disappear. The strict experimental proof of this conclusion can only be obtained by a great number of experiments with a very concentrated liquid, or by means of a direct experiment, in which we begin with pure oxygen and for each decrease of temperature add the necessary quantity of nitrogen [1]).

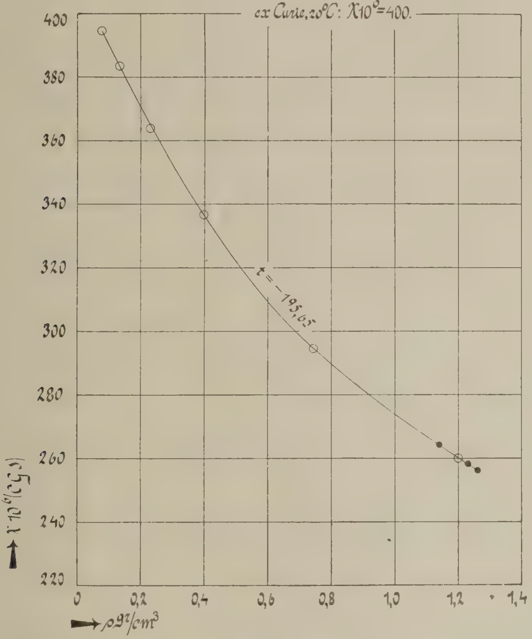

Fig. 3.

§ 4. *Theoretical conclusions.* We must call attention to the fact that every theoretical interpretation of our results must account for two different facts: in the first place for the change of the magnetisation with the density, and in the second place the parallellism of the lines $\frac{1}{\chi} = f\,(T)$.

It is plain that **Langevin**'s *theory, only supplemented by the hypothesis of the negative molecular fields, is sufficient to give the*

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[1]) Experiments make it probable, that for gaseous oxygen χ even at —183° C. does not deviate or at least (see the conslusion of § 4) deviates only very little from **Curie**'s law. In the application of the ascension method χ may therefore not be supposed to be equal for the liquid and for the vapour, as was done in formula (2) of Comm. No. 116, but a correction must be applied, which, however, in our case remains within the limits of experimental error.

explanation. In fact if N represents the coefficient of the molecular field, it leads to the law

$$\frac{1}{\chi} = \frac{T}{C} + N\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$\chi\,(T + \Delta) = C, \text{ where } \Delta = C\,N\rho,$$

which agrees with the law following from Table II, if we assume that Δ or $N\rho$ *decreases with the density.*

This being established, the experiments further permit, and this gives them an additional significance, to account for *the way in which the molecular field changes with the density or with the distance of the molecules.*

We remark in the first place, that the accurate calculation of the molecular fields rests upon the knowledge of the *deviations from* CURIE's *law*, and not upon that of the susceptibilities themselves (formula (1)). It would therefore be necessary to know the specific magnetisations in absolute value down to at least 0.1 $^0/_0$ in order to be able to deduce the fields from them with sufficient certainty; this is especially the case for the great dilutions where the deviations are extremely small. A determination of this degree of accuracy demands in itself a long and difficult special investigation with perfected apparatus.

The solution, if not completely found, may yet be brought within narrow limits. The first question that then arises is, whether the field is equal to a particular power of the distance of the molecules i. e. of the density. If we suppose $N = a\rho^n$, then the molecular field is $a\rho^{n+1}$. At constant temperature $^1/_\chi = f(\rho)$ is then a parabola of the degree $n + 1$, with the axis vertical and the top on the axis of ordinates. For $n = 0$, $^1/_\chi$ is represented by a straight line.

In Fig. 4, the curve which our experimental data give for the temperature 77°.45 K. is shown; it deviates from the straight line, but the deviations are not much greater than the errors of observation, except for the most diluted mixture. Moreover the slight curvature is *in the opposite sense to all the parabolae for which* $n > 0$. The observations at concentrations smaller than 0.1 indicate that the molecular field then begins to change more quickly, but they do not justify the assertion that this is actually the case It is therefore not probable that the results can be represented by means of a positive n (except for very great dilutions, for which we have not a single indication); in order to elucidate this point we have also constructed the curve $^1/\chi = f(\rho)$ which with the same extremities corresponds to $n = 1$, i. e. to the law that the molecular field would be proportional to the square of the density or to the inverse sixth power of the mean distance of the molecules; it is obvious that this bears no resemblance to the experimental curve.

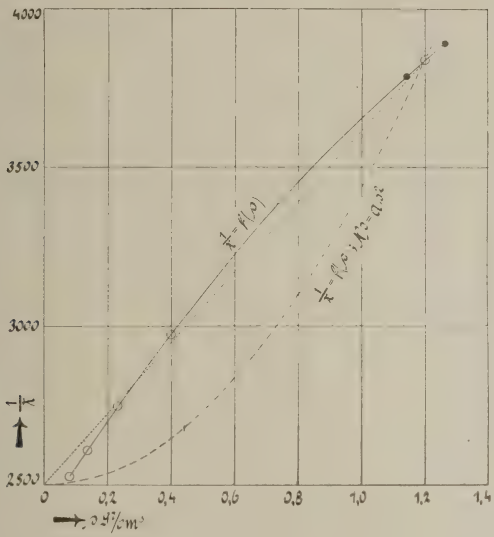

Fig. 4.

We assume therefore *that the molecular field of oxygen changes about proportionally to the density* [1]).

This law, in the case of the appearance of a negative field (assuming that this exists) for oxygen, differs totally from that at which WEISS arrived, in the case of the positive molecular field with alloys of ferromagnetic metals, for the dependence of N upon the density, and from which he inferred influences according to the inverse sixth power of the distance, which for that reason we have just referred to. (From our law, in the same way, an influence according to the inverse third power of the distance would follow.)

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[1]) Cf. the next paper by KAMERLINGH ONNES and OOSTERHUIS, in which the idea of the dependence of Δ on the concentration is extended to the "atomic concentration" of the paramagnetic component in crystallized compounds, in the first place in those containing water of crystallization.

At present, we need not see any contradicton between these two results, as the conditions for which the two laws of distance hold good, are quite different. This applies both to the nature of the substances and to the state of aggregation in which they were examined. Moreover it must be particularly borne in mind that the sign for the molecular field is different in both cases. The part of the curves referring to the change of N with the concentration, which Weiss makes use of in his theory, lies entirely in positive fields, the transition to negative fields is curved. We are in complete ignorance as to the origin of the mysterious influences which cause the phenomena ascribed to the molecular field. There is no ground therefore to expect that both fields are subject to the same law. Should it be confirmed that both kinds of molecular field depend upon the distance of the molecules according to different laws, we might even see in this a proof that in both cases influences are at work which are the effect of different causes[1].

If we continue the idea that the deviations from Curie's law are to be attributed to a negative field, we come with the value 0.03152 which we deduce for Curie's constant, to 14.11 magnetons per molecule of 2 rigidly connected atoms, while Weiss and Piccard, from their determination of the constant for gaseous oxygen arrive at exactly 14. An error of 0.2 degrees in the lowest temperature at which we took observations would explain this difference. There is therefore no reason to take this observation as at variance with the law of magnetons. [At the end of

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[1] The function $\rho^{4/3}$, which was given in a preliminary note (Soc. Suisse de physique, Frauenfeld 1913) was based upon data which later appeared to have been insufficient in number, and before some subsequently calculated corrections had beed applied. The function may be correct for a range of weak concentrations.

§ 4 we have drawn attention to a circumstance that would possibly explain the difference. Added in the translation.]

Although the hypothesis of the negative molecular field is sufficient to describe the phenomena, it is not devoid of interest to consider in how far the other hypotheses can be reconciled to the observations.

As regards the polymerisation-hypothesis, it is not probable that the association decreases as rapidly with the density at constant temperature as would have to be the case if the experiments were to be explained by it, nor that the result of a given form of the hypothesis, which might give this change, would lead to the set of parellel straight lines in fig. 2.

Oosterhuis's hypothesis, that the energy of rotation should take the form of

$$U_{\mathrm{r}}=\frac{h\nu}{e^{\frac{h\nu}{kT}}-1}+\frac{h\nu}{2}$$

needs to be supplemented by a further hypothesis. It is in the line of the deduction to accept that the moment of inertia of the molecule changes considerably by dilution, and increases to very great values. Even in accepting this hypothesis it appears from calculations by Dr. Oosterhuis that the deviations of the curves calculated from the set of the parallel straight lines in fig. 2 are too large to be explained by experimental errors ¹).

Finally we may remark that the supposition

$$1/\chi = f(T) + N\rho \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

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¹) In these calculations Oosterhuis started from the values of Δ which were deduced immediately from the experiments according to Table II, which in particular gives the most probable slope of the straight lines accepted to be parallel. Since then Dr. Keesom has communicated to us that by calculating the values of Δ in giving to $f(T)$ [see formula (3)] either Oosterhuis's form, or the form which Keesom has developed in Suppl. N⁰. 32*a*, whereby the values of Δ are a little changed, one obtains a satisfactory representation. The values of Δ are then in agreement with the function $\rho^{2/3}$ for large values of ρ, which he arrives at (see a paper of his to be published shortly). In his calculations Keesom accepted the number of magnetons of Weiss and Piccard. His theory explains also that the curve $1/\chi = f(\rho)$ of fig. 4 does not pass through the origin. [Note added in going to press.]

combines the various hypotheses which we have explained above (except that of polymerisation), and agrees with our experiments if $f(T)$ is independent of the density, and N of the temperature [1]). It accounts for all phenomena which are expressed by a parallel displacement whatever value is ascribed to $f(T)$, if only it remains independent of the density.

[One can imagine that $f(T)$ is in reality of such a form that in the temperature-range of our experiments it gives for χ of the oxygen in the liquid mixtures of oxygen and nitrogen a value which, while being small for the large densities of oxygen, increases in passing to more and more high dilutions, and approaches in the limit to a value *greater* than that which with CURIE's law is obtained from WEISS and PICCARD's experiments. If further experiments which may be undertaken with a view to throwing light upon this point should give a positive result one could explain without relying upon experimental error the slope of our lines for $^1/_\chi$ being a little small (given by $C = 0.0315$, see fig. 2). It would then be of interest to compare that result with what the investigation by KAMERLINGH ONNES and OOSTERHUIS on the susceptibility of gaseous oxygen at low temperatures will teach when extended to lower temperatures. It is not entirely excluded that the nitrogen plays a different part from a vacuum. Added in the translation.] (Cf. note 1 p. 53. Added in going to press).

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[1]) $f(T)$ represents the energy of rotation as a function of the temperature (3) is only applicable to the range where the magnetisation is strictly parallel to the field. Formula (3) includes inter alia the vanishing of the CURIE point in ferromagnetic substances caused by zero energy deduced by KEESOM (Leid. Comm. Suppl. N⁰. 32 *a* and *b* 1913).

[Regarding the influence of the density on $f(T)$ in KEESOM's theory see his next paper, cf. also note 2 p. 6 of Suppl. N⁰. 32*a*. Added in going to press.]

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 139^e.

* * *

H. KAMERLINGH ONNES and E. OOSTERHUIS.
Magnetic researches. XIV. On paramagnetism at low temperatures. (Continuation of VII.)

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, 28 **Februari 1914**, p. 1033—1037).

Eduard IJdo — Printer — Leiden.

H. KAMERLINGH ONNES and **E. OOSTERHUIS**. *Magnetic researches. XIV. On paramagnetism at low temperatures.* (Continuation of VII).

§ 15. *Ferrous sulphate.* (Continuation of III § 2). The measurements of the susceptibility of paramagnetic substances at low temperatures were continued according to the method previously described.

Crystallized ferrous sulphate, which had been already investigated by KAMERLINGH ONNES and PERRIER (Comm. N⁰. 122*a*), was once more very carefully prepared, by precipitating it out of its aqueous solution with alcohol. The values of the susceptibility found do not entirely correspond to the previous ones, but the dependence on the temperature is precisely the same, as is shown by the following table, when compared with table II of Comm. N⁰. 122*a*.

TABLE XII.

Crystallized ferrous sulphate $FeSO_4 . 7H_2O$ precipitated with alcohol.			
T.	$\chi \cdot 10^6$	$\chi . T . 10^6$	Bath.
292.°3 K.	42.4	12390	in air
77. 3	160	12370	liquid nitrogen
64. 6	191	12340	
20. 3	571	11590	liquid hydrogen
14. 7	756	11110	

§ 16. *Palladium.* Pure palladium (from HERAEUS) gave the following figures:

TABLE XIII.

Palladium.		
T	$\chi \cdot 10^6$	Bath
291° K.	5.3	in air
250	5.8	liquid methyl chloride
212	6.0	
170	6.9	liquid ethylene
77.3	8.1	liquid nitrogen
70.2	8.2	
64.6	8.3	
20.3	9.9	liquid hydrogen
17.9	10.2	
14.7	10.9	

Palladium, it will be seen, deviates markedly from CURIE'S law. CURIE found just for this substance the law $\chi . T = \text{const.}$ fairly well confirmed. HONDA [1]) (above ordinary temperature) and OWEN [2]) (below ordinary temperature down to 100° K) found deviations from CURIE'S law which agree very well with our results. The line $\frac{1}{\chi} = f(T)$ shows some irregularities which are greater than we should have expected considering the degree of accuracy of the experiments.

§ 17. *Ferric ammoniumsulphate (iron alum).*

This substance will be seen to follow CURIE'S law throughout

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[1]) K. HONDA. Ann. der Phys. 32, p. 1027. 1910.

[2]) M OWEN. Ann. der Phys. 37, p. 657. 1912.

TABLE XIV

Ferric ammoniumsulphate $Fe_2\ (SO_4)_3 .\ (NH_4)_2SO_4 + 24H_2O$.

T.	$\chi \cdot 10^6$	$\chi \cdot T . 10^5$	Bath
290.°0 K.	30.4	882	in air
169. 6	51.8	879	liquid ethylene
77. 3	114.7	887	liquid nitrogen
64. 6	137.0	885	
20. 4	432	881	liquid hydrogen
17. 9	492	881	
14. 7	598	879	

the whole range of temperature that was examined. This, according to the theory developed by Oosterhuis in Suppl. N^0. 31, would be owing to the great moment of inertia which a molecule of this substance undoubtedly possesses.

It may also be explained by the theory which Foëx gives following Weiss (C. R. t. 157, p. 1145, 1913). In fact iron alum is a substance crystallizing in the regular system and according to Foëx, for such substances the line $\frac{1}{\chi} = f(T)$ will be a straight line at all temperatures:

This property of ferric alum may also be regarded from another point of view if we consider the latest results by Kamerlingh Onnes and Perrier (Comm. N^0. 139*d*). In § 3 we pointed out that interposition of water molecules between the molecules of ferrous sulphate, as occurs when this salt crystallizes with water of crystallisation, causes the deviation from Curie's law to disappear, and thus diminishes Δ. We found the same in § 10 for manganese sulphate, and in § 11 we came to the conclusion that the decrease of Δ might be the consequence of an increase in the distance of the paramagnetic constituents of the salt. Finally we drew attention to the fact that the transition of oxygen from the gaseous to the liquid form might be accompanied by a change in Δ. Perrier and Kamerlingh Onnes have now demonstrated that Δ decreases with the dilution of oxygen with nitrogen, and that the change of Δ with the density, which must be assumed to find for liquid oxygen at all temperatures [with the help of the $\Delta_{\rho\, liq\, T}$ corresponding to the liquid density $\rho_{liq\, T}$ from

$$\chi\,(T + \Delta_{\rho\, liq\, T}) = C]$$

the same number of magnetons as in the gas at ordinary temperature, agrees well with the change of Δ with the distance of the molecules, which is found from the dilution of oxygen with nitrogen. By this it has become evident that if Δ is the consequence of the existence of a molecular field, this field decreases when the molecules are brought to a greater distance from each other, and soon, at molecular concentrations of about $\frac{1}{200}$, is no longer perceptible.

In ferric alum, the distance of the Fe-atoms is of the same order as that at which the molecular field of the oxygen molecules in the solution of oxygen and nitrogen disappeared in Kamerlingh Onnes and Perrier's experiments. That this substance conforms to Curie's law as far down as the freezing-point of hydrogen, may therefore be due to the atoms of iron, at the *atomic concentration* in this substance, being at a distance which permits them to behave like those of a normal paramagnetic substance. Should this hypothesis be correct, it would be of importance to take notice of the atomic concentration, in studying paramagnetic substances. To determine the number of magnetons in a paramagnetic atom, we should therefore have to take (complex) compounds, which fulfil this condition of being sufficiently "diluted". This condition is fulfilled by many of the materials which have been used for the calculations about magnetons ^{1}).

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1) In ferric alum is realised a case of solution of a paramagnetic in a practically neutral substance, of the same kind as that which Weiss considered by extrapolation in his discussion of the ferro-magnetic alloys when he was searching for the law of distance for the molecular field.

If we arrange the substances according to the value of their atomic concentration, we see that in general the deviations from CURIE's law at low temperatures seem to appear sooner in substances with a high concentration. OOSTERHUIS's calculations (Comm. Suppl. N⁰. 31) give particulars of the amount of the deviation in different substances. It will therefore be desirable, if we want to determine the number of magnetons in an atom at low temperature, to go down to very small concentrations. This is no difficulty for the measurement, for, although the specific susceptibility at small concentration is small, it increases considerably according to CURIE's law for a given concentration with the transition to low temperatures. We should come upon chemical ground if we were to discuss what compounds would be suitable for this purpose. Double salts and complex compounds seem to be particularly suitable, provided we are able to apply the correction for diamagnetism.

It is very likely that with high atomic concentrations Δ may rise to very high values. Something of this sort might be the case with platinum (see § 12) and with the ferromagnetic substances the investigation of which first led WEISS and FOËX to the introduction of a negative magnetic field.

For crystals, a "*linear concentration*" may have to be introduced. The value of Δ for different directions, would have to be brought into connection with this.

In the further study of the deviation from CURIE's law, use will have to be made of the results of WERNER's investigation of the constitution of complex compounds on the one hand, and on the other hand of the data which experiments upon the diffraction of RÖNTGEN rays, such as BRAGG in particular has made, may yield. What these can teach concerning the arrangement of the atoms and the structure of the atomic lattice, is of great importance from the above point of view.

(*To be continued*).

Errata Communication N⁰. 139*f*.

Title-page: in the title: for Experimonts read Experiments.
after 28 Februari insert 1914.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory

N°. 139^f.

H. KAMERLINGH ONNES. Further Experiments with Liquid Helium. I. The HALL-effect, and the magnetic change in resistance at low temperatures. IX. The appearance of galvanic resistance in supra-conductors which are brought into a magnetic field, at a threshold value of the field.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **28 Februari**, p. 1027—1033).

EDUARD IJDO. — PRINTER — LEIDEN.

p. 65 line 2 from the bottom: for imperceptible read of no importance.

H. KAMERLINGH ONNES. *Further Experiments with Liquid Helium. I. The* HALL-*effect, and the magnetic change in resistance at low temperatures.* IX. *The appearance of galvanic resistance in supra-conductors which are brought into a magnetic field, at a threshold value of the field.*

§ 1. *Introduction, first experiments.* In my last paper upon the properties of supra-conductors, and in the summary of my experiments in that direction which I wrote for the Third International Congress of Refrigeration in Chicago (Sept. 1913, Suppl. N^0. 34*b*), I frequently referred to the possibility of resistance being generated in supra-conductors by the magnetic field. There were, however, reasons to suppose that its amount would be small. The question as to whether the threshold value of the current might be connected with the magnetic resistance by the field of the current itself becoming perceptible could be answered in the negative, as we had then no reason to think of a law of increase of the resistance with the field other than proportional to it, or to the square of it, and the law of increase of the potential differences at currents above the threshold value could not be reconciled with either supposition. A direct proof that in supra-conductors only an insignificant resistance was originated by the magnetic field was found in the fact that a coil with 1000 turns of lead wire wound within a section of a square centimetre at right angles to the turns round a space of 1 c.M. in diameter remained supra-conducting, even when a current of 0.8 ampère was sent through it. The field of the coil itself amounted in that case to several hundred gauss, and a great part of the turns were in a field of this order of magnitude, without any resistance being observed. The inference was natural, that, even if we should assume an increase with the square of the field, the resistance would probably still remain imperceptible even in fields of 100 kilogauss. In my publication (see Report Chicago, Suppl.

N⁰ 34*b*) I restricted my conclusion about the resistance in the magnetic field to a limit of 1000 gauss, and I also remarked that when it came to making use of the supra-conductors for the construction of strong magnets without iron, it would be necessary in the first place to investigate what resistance the magnetic field would generate in a supra-conductor, and I immediately prepared experiments in connection with this. That I was firmly convinced that the action would be only small, is shown by the fact that I arranged the apparatus for these experiments as if for a phenomenon that could only be studied with profit in fields of 10 kilo-gauss, but it now appears that even then without further preparation, I might have made the observations described below quite easily with the field of 2 kilo-gauss that I then had at my disposal.

For our experiments a coil was prepared as described above, but wound non-conductively. When (17 January 1914) it was brought into a field of 10 kilo-gauss, it showed a considerable resistance. We had not been so successful in the construction of this coil as in the previous one, as it did not become supra-conducting. It was therefore possible that not much value could be attached to this experiment. A coil with tin wire prepared in the same way as the above described non-inductive lead coil also showed a considerable resistance in a field of 10 kilo-gauss when cooled to 2° K., which decreased more slowly than proportionally when the field was reduced to 5 kilo-gauss. In this case again we had not succeeded in making the coil so that it would become supra-conducting, but (always assuming a regular decrease with the field, and supposing that the fact that the coil did not become supra-conducting only gives a non-essential disturbance) the results of both experiments did not seem to be reconcilable with the above mentioned observations, in which the magnetic field generated no resistance in supra-conductors.

The first thing to do was therefore to repeat the experiments with the coils of tin and lead, which had become supra-conducting in the former experiments, notwithstanding that the windings were in a magnetic field. That these coils were not wound induction-free, was of no consequence, now that it was a question of such comparatively large resistances.

p. 66 line 17 from the top: for non-conductively read non-inductively.

§ 2. *Further experiments with lead and tin which show a sudden change in the resistance at a threshold value of the magnetic field.*

The lead coil of Table XII Comm. N^0. 133, as it was not wound induction-free, was placed in the cryostat of the apparatus to be described in a future paper for magnetic measurements in liquid helium, so that the plane of the windings coïncided with the lines of force of the magnetic field which is to be applied. This last acts therefore partly transversely upon the conductor (lines of force at right angles to the current), partly longitudinally (lines of force in the direction of the current).

It was first ascertained that the coil was supra-conducting at the boiling-point of helium. Further that it remained supra-conducting when a current of 0.4 ampère was sent through it; even then the windings were in a not inconsiderable field of their own current.

For further confirmation it was ascertained that the current actually passed through the windings by bringing a small cardanically suspended magnet (pole-seeker) near the cryostat; it showed the movements which were to be expected.

Then the magnetic field was applied. With a field of 10 Kilo-gauss there was a considerable resistance, at 5 Kilo-gauss it was somewhat less. This made it fairly certain that the magnetic field created resistance in supra-conductors at larger intensities, and not at smaller ones. The apparent contradiction that so far had existed between the different experiments, was hereby solved. Later it appeared that 500 gauss was below the threshold value, and 700 above it. Further investigation gave for the resistance (expressed in parts of the resistance at 0° C) as function of the field, the curve that is given diagrammatically completed in fig. 1. The numerical values, in so far as they are necessary

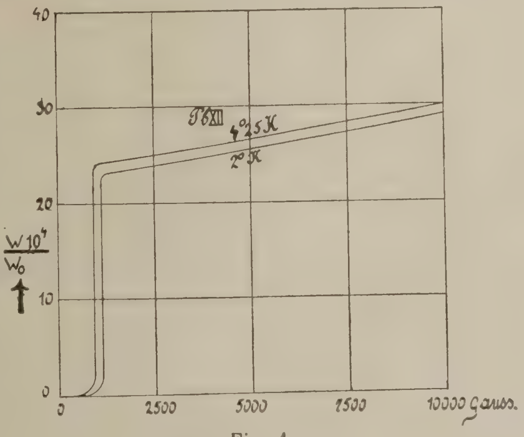

Fig. 1.

for the description of the phenomenon, can be read from the figure, so that they need not be separately detailed here.

It will be seen that the transition from the supra-conducting condition to the ordinary conducting condition through the magnetic field takes place fairly suddenly. The curve, which represents the change of the resistance with the field is closely analogous to that which represents the change of the resistance with the temperature (comp. $I = 0.004$ amp. in fig. 7 in Comm. N°. 133). The resistance measurements were made with a current of 0.006 ampère. Of the two curves in fig. 1, one refers to 4°.25 K, and the other to 2° K. The sudden change in the resistance moves at low temperatures towards higher fields; beyond this point the resistance increases at lower temperatures (2° K) almost in the same way as at higher ones, it seems as if *the introduction of the magnetic field has the same effect as heating the conductor.*

The tin coil of Comm. N°. 133 Table IX was examined in the same way. With this too we have a result in which longitudinal and transverse effects are combined. At 4°25 K the tin is still in a state of ordinary conductivity, the curve, which represents the resistance as a function of the field decreases in steepness (see fig. 2) with a diminishing field and meets the axis of ordinates pretty nearly parallel to the axis of abscissae. The only thing, therefore, that is remarkable here as compared to what is observed at higher temperatures, is the decrease of the slope to zero. There is no indication of a sudden change.

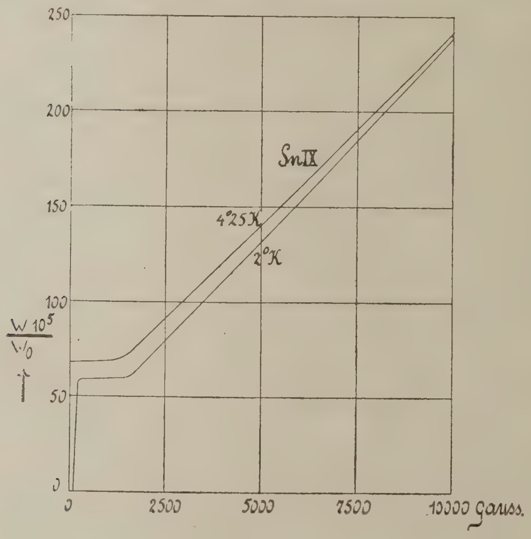

Fig. 2.

With the supra-conducting tin at 2° K we find, as with lead,

p. 69 in Fig. 3 for 1000 read 10000.

line 21 from the bottom: for W_{Pbft} read W_{Pbf1}.

a sudden change, in this case at the threshold value of 200 gauss. In fact with tin at 2° K we are much nearer to the temperature of sudden change for the resistance (3°.8 K) than in the case of lead (sudden change at 6° K (?), comp. Comm. N^0. 133).

§ 3. *Separate observations of the longitudinal and of the transverse effect with lead.*

Pressed lead was wound on a plate, so as to cover it with a few flat layers of insulated windings. The windings could be so directed that the effect was entirely transverse, or almost entirely longitudinal. The results for the temperatures of 2° K and 4°.25 K are given in the four curves in fig. 3.

The sudden change in both effects takes place almost at the same threshold value of the field. The longitudinal effect is weaker than the transverse effect. The value of the effect at hydrogen temperatures was examined by Dr. K. Hof and myself, and I take this opportunity to thank him for his help. A paper on the subject will be published shortly. It appears from this that the effect which (see fig. 3, and in detail fig. 4) changes little with the fall from 4°.25 K to 2° K, increases considerably with the fall from 14° K to 4°.25 K.

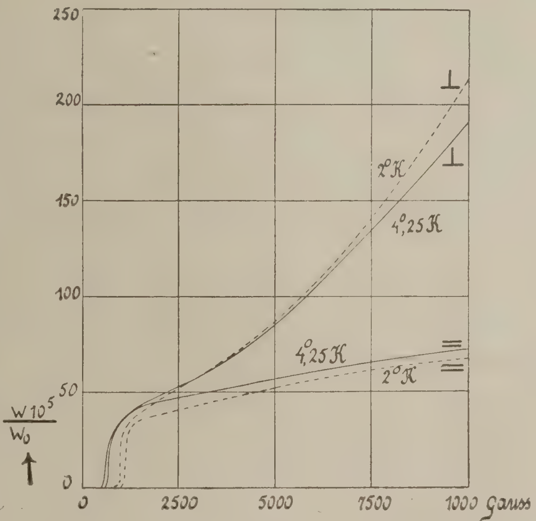

Fig. 3.

It is worthy of notice that the sudden change *differs considerably in magnitude* with Pb_{XII} and Pb_{f1}. Possibly there is a difference in the nature of the lead in the two coils. In fact at 20° K.

$$\frac{W_{PbXII}}{W_0} = 0.0284 \text{ and } \frac{W_{Pbft}}{W_0} = 0.0274.$$

Amongst the different questions that arise, one is whether an lead wire might be constructed in which the magnetic resistance, remaining zero as far as the threshold value of the field, will further gradually increase with the field from the value 0 upwards.

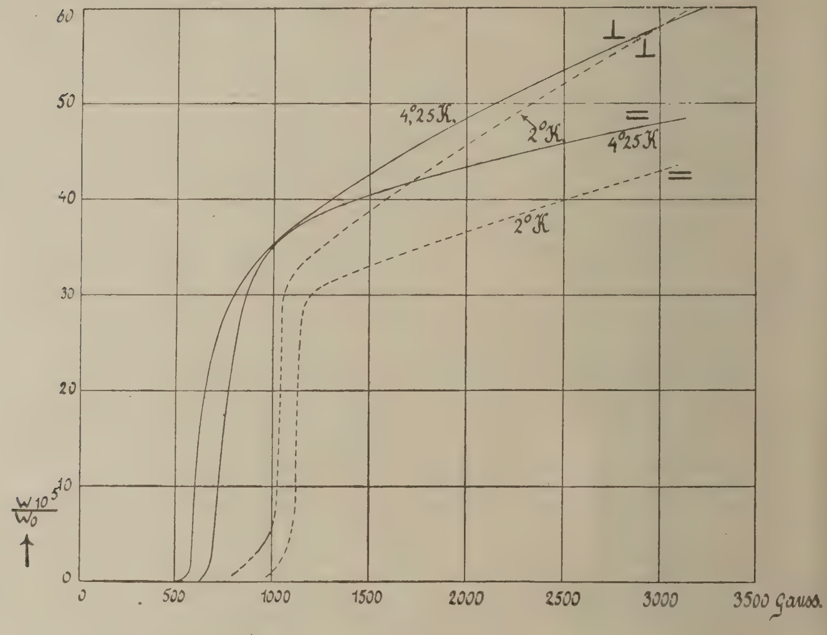

Fig. 4.

There is no doubt that the phenomenon discovered here is connected with the sudden appearance of ordinary resistance in the supra-conductors at a certain temperature. The analogy between the influence of heating upon the resistance and that of the introduction of the magnetic field, is so far complete.

One would be inclined to assume that an energy of rotation determined by the magnetic field might be simply added to the energy of the irregular molecular motion. If in the production of the obstructions which determine the resistance we have to do with dissociations in the sense, that movements of electrons in certain paths become unstable at a definite temperature, the magnetic centrifugal force might make there motions one-sidedly unstable at another temperature.

p. 70 line 2 from the top: for an read a.
line 2 from the bottom: for there read these.

If the creation of ordinary resistance in supra-conductors with currents above a certain threshold value, which is fully described in Comm. N⁰. 133, really is a peculiarity of the supra-conducting metal, and not due to disturbances, then the new phenomenon might also be connected with this property. In fact if it were once proved — to use an image already introduced into my paper for the Congress in Chicago — that the vibrators which cause the resistance can only be set in motion when the stream of electrons passes them with sufficient rapidity, then it would not be surprising that the magnetic resistance does not arise until the rapidity of the circulating motions of the electrons is great enough to carry the atoms with it and set them in rotation, by which they can then disturb the regular motion of the electrons.

Finally, it is certain that the phenonenon described is connected with the laws of magnetisation of supra-conductors which are as yet unknown.

Before however drawing definite conclusions from the new phenomenon, it is desirable to gather more experimental information on the subject.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 140ª.

◆

C. A. CROMMELIN. Isothermals of monatomic substances and their binary mixtures. XVI. New determination of the vapour-pressures of solid argon down to —205° C.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam,* **28 Maart 1914**, p. 1212—1215,

Eduard IJdo. — Printer — Leiden.

C. A. CROMMELIN. *Isothermals of monatomic substances and their binary mixtures.* XVI. *New determination of the vapour-pressures of solid argon down to* —205° C.

The vapour-pressures of solid argon which are communicated below form an extension of and have partly to replace those published on a former occasion [1]).

The measurements were made in the usual vapour-pressure apparatus for low temperatures [2]).

The manometer on which the pressures were read was constructed after the model used by G. Holst for his measurements on ammonia and methyl-chloride to be published shortly: this form of manometer gives perfect security against leakage.

The method of conducting the measurements gives no occasion for special remarks: we refer the reader to the previous paper.

It may be mentioned however, that the temperatures were measured with a gold-resistance thermometer, as below —200° gold is preferable to platinum. This thermometer was very carefully compared with the standard-platinum-thermometer Pt_{I}'.

I am indebted to Mr. P. G. Cath, assistant in the physical Laboratory, for the measurement and calculation of the temperatures and for the comparison of the resistance-thermometers referred to.

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[1]) C. A. Crommelin. Comm. N^0. 138*c*. The measurements were repeated because shortly after the publication doubt arose as to the accuracy of the determinations at the lowest temperatures (see note on p. 23 of Comm. N^0. 138*c*). The new measurements showed this doubt to be justified, the observation at — 206°.04 being found altogether wrong and the one at — 197°.62 not very accurate. The remaining observations of Comm. N^0. 138*c* correspond well to those published here. The probable cause of the errors must be air leaked into the argon at the low pressures: but I cannot explain how it is that this was not noticed during the measurements.

[2]) H. Kamerlingh Onnes and C. Braak, Comm. N^0. 107*a*.

Table I contains the results of the observations and the deviations from the Rankine-Bose-formula

$$\log p_{\text{coex}} = a_{\text{RB}} + b_{\text{RB}}\, T^{-1} + c_{\text{RB}}\, T^{-2} + d_{\text{RB}}\, T^{-3},$$

with the following values for the coefficients

$a_{\text{RB}} = + 6.6421$ $c_{\text{RB}} = - 0.67743 \times 10^4$
$b_{\text{RB}} = - 3.7181 \times 10^2$ $d_{\text{RB}} = + 0.28034 \times 10^6$

and from Nernst's formula (treated simply as an empirical formula)

$$\log p_{\text{coex}} = \frac{A}{T} + BT + D \log T + C$$

with the coefficients

$A = - 567.49$ $C = + 20.851$
$B = + 0.010899$ $D = - 6.9057.$

The values of the coefficients in both formulae hold for p in cms. mercury.

TABLE I.

Vapour-pressures of solid argon.

Date 1913	N^0.	θ (Celsius in Kelvin-degrees).	p_{coex} in atm. int.	p_{coex} in cms. mercury.	Percentage deviations from	
					Rankine-Bose formula.	Nernst formula.
Nov. 26th	XXIII	— 189.64	0.6554	49.78	+ 0.20	+ 1.33
	XXIV	191.31	0.5175	39.30	— 0.19	— 0.11
	XXVI	195.60	0 2749	20.88	+ 0.35	— 1.33
	XXVII	197 25	0.2153	16.35	+ 2.16	+ 0.15
Nov. 28th	XXVIII	200.97	0.1113	8.456	— 0.94	— 2.27
	XXIX	202.21	0.08931	6.783	— 0.89	— 1.49
	XXX	203.78	0.06740	5.119	— 0.04	+ 0.59
	XXXI	205.32	0.05043	3.830	+ 0.36	+ 2.79

The comparison with the formula which SACKUR has deduced from NERNST's heat-theorem

$$\log p = -\frac{\lambda}{2.3\,RT} + \frac{c_p}{R}\log T - \frac{1}{2.3\,R}\int_0^T \frac{c}{T}\,dT + C + \frac{c_p}{2.3\,R}$$

is given in table II.

TABLE II.

ϑ	$p(O)$	$p(C)$
−189.64	0.655	0.618
191.31	0.518	0.507
195.60	0.275	0.286
197.25	0.215	0.226
200.97	0.111	0.141
202.21	0.089	0.124
203.78	0.067	0.107
205.32	0.050	0.094

For details as to the manner in which the various values have been calculated the reader is referred to the previous paper. It will be seen that the agreement is satisfactory at the higher temperatures, while at the lower temperatures the deviations become very large.

Finally I have calculated the heat of sublimation of solid argon from the simplified CLAPEYRON-CLAUSIUS-formula

$$\lambda_{\text{sol.-vap.}} = \frac{RT^2}{p}\left(\frac{dp}{dT}\right)_{\text{coex.}}$$

Calculating $\left(\frac{dp}{dT}\right)_{\text{coex.}}$ from the above RANKINE-BOSE-formula the following values are found for the heat of sublimation expressed in calories per gramme of substance at the various observation temperatures.

TABLE III.
Calculated heat of sublimation of argon.

θ	$\lambda_{\text{sol.}-\text{vap.}}$
— 189.64	47.36
191.31	47.16
195 60	46.58
197 25	46 31
200.97	45.59
202.21	45.32
203.78	44.93
205.32	44.51

In concluding I am glad to express my hearty thanks to Professor H. Kamerlingh Onnes for his continued interest in my work.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

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BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 140^b.

◆

H. KAMERLINGH ONNES. Further experiments with liquid helium. J. The imitation of an AMPÈRE molecular current or of a permanent magnet by means of a supra-conductor.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **24 April 1914**, p. 1413—1421.)

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES. *Further experiments with liquid helium. J. The imitation of an* AMPÈRE *molecular current or of a permanent magnet by means of a supra-conductor.*

§ 1. *Introduction.* If a current is generated in a closed supra-conductor, from which no other work is required than what is necessary to overcome the possible remaining micro-residual resistance of the conductor, it follows, from the small value that the micro-residual resistance can have at the most, that the current will continue for a considerable time after the electromotive force that set it in motion has ceased to work. The time of relaxation τ in which the current decreases to e^{-1} th of its value is given by the ratio $\frac{L}{r}$ of the self-induction L and the resistance r of the circuit. When r approaches zero, this period may rise to very high values. Whereas the time of relaxation is extremely small in ordinary cases (for the coil with which we are about to deal for instance, of the order of a hundredthousandth of a second) when the resistance in the supra-conducting condition becomes say 1,000,000 or even 1,000,000,000 times smaller it may increase so much, that the disappearance of the current can be observed; it may even take place extremely slowly.

From the moment that I had found in mercury a supra-conductor at the lower temperatures which can be obtained with liquid helium, I was desirous to demonstrate the persistence of a current in a conductor of this kind, and amongst other things to take advantage of it in the further investigation of the micro-residual resistance of the supra-conductor [1]). But it was only after the previous study of various problems, which were also of value for the knowledge of the conditions which had to be considered, that I arrived at the simple experiment which I am now able to describe, and which confirms what I have adduced in a convincing way.

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[1]) For the sake of brevity we use the word resistance here in the sense of quotient of potential difference and current strength. In supra-conductors (see Comm. N⁰. 133) we can at present only speak of current and potential difference; whether the relation between these two can be expressed by means of the conception of specific resistance, has still to be investigated. [Comp. note 1 § 3].

For this experiment a conductor was available whose constants, in so far as they were needed in designing the experiment, were known: I refer to the coil of lead wire Pb_{XII} which has several times been mentioned in previous papers. A thousand turns of lead wire of $\frac{1}{70}$ sq. mm. in section are wound on a small brass tube of 8 mm. in diameter in a layer 1.1 cm thick and 1.1 cm long. At the ordinary temperature the coil has a resistance of 734 Ω and as the inductance is 10 milli-henries, the relaxation-time may be put at about 1 : 70000 of a second. The micro-residual resistance at 1.°8 K. had been found to be more than 2×10^{10} times smaller than the resistance at the ordinary temperature; the relaxation-time therefore must be at least of the order of a day. The limit to which the current may be raised before ordinary resistance is suddenly generated, had also been determined; at 1.°8 K this limit was 0.8 amp.; it is clear that a lower current than that is sufficient to make the coil into a powerful little magnet. Finally the threshold value of the magnetic field, below which no resistance is produced in the coil was known: at 1.°8 K it had been found to be about 1000 gauss. It was ascertained (cf. § 3), that it was unnecessary to use a field of that strength to be able to make the experiment by means of generating a current by induction in the conductor. The conductor after having been tested as to its superconductivity had to be closed in itself in a superconductive way. This was effected by fusing the ends of the lead wire together: in previous experiments it had been found, that this treatment did not lead to the production of ordinary resistance. In view of all the data I could be assured, that all the conditions necessary for the success of the experiment were fulfilled.

§ 2. *Arrangement of the experiment.* The coil was fitted up in the same cryostat which had served for the previous experiments with the plane of the windings vertical in such a manner, that it could be raised and lowered, as well as turned round a vertical axis. Fig. 1 shows the arrangement diagrammatically.

As the coil was closed the current in it was generated by induction A large Weiss-electromagnet at hand for the experiments of Comm. N⁰. 140*d* could be moved on casters towards the cryostat to a position in which the cryostat with the coil was in the interferrum.

In order to obtain an unambiguous result it is advisable to be able to test the magnetic condition of the coil while no other magnetic objects are in the neighbourhood; it is also necessary to prevent the induction currents which are generated when the field is produced and when it disappears from partly or completely neutralising each other (cf. § 4).

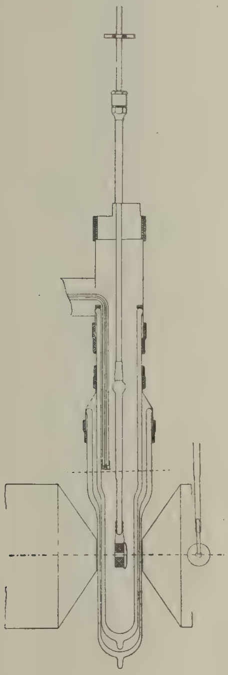

Fig. 1.

It can therefore be easily seen that the following procedure is advisable: the field is put on, while the coil is in the cryostat at the centre of the interferrum, everything being prepared for siphoning the liquid helium into the cryostat. The current generated at the production of the field is then immediately dissipated by the ordinary resistance of the coil before the helium is poured over. Care is taken to keep the field below the threshold-value of the production of ordinary resistance, which holds for the temperature at which the experiment is going to be made. The coil is then cooled by letting in liquid helium, the field remaining unchanged. In this manner a supra-conducting coil is obtained, closed in itself without a current placed in the magnetic field. If the field is now put off and the apparatus which have produced it are removed, a current will remain in the coil which is smaller than or in the limit equal to the threshold-value corresponding to the temperature of the coil. The presence of this current can be established by its magnetic action outside the cryostat.

In order to obtain a strong current it is advisable to cool the coil as far down as possible, as thereby the threshold-value of the field to be used for the induction and the threshold-value of the current are both made as high as possible. For that reason the first experiment was made at a temperature of 1.°8 K, the lowest temperature which can be reached comparatively easily and maintained for a long time.

§ 3. *Calculation of the experiment.* Assuming that the field diminishes proportionally to the time t from H_0 to 0 and calling M the magnetic potential of the coil in the field H, $\frac{dM}{dt}$ will be constant during the period of the disappearance of the field and the equation [1]

$$L\frac{di}{dt}+r\,i=\frac{dM}{dt}$$

with $i=0$ at the beginning gives

$$i=\frac{1}{r}\frac{dM}{dt}\left(1-e^{-\frac{r}{L}t}\right),$$

and for small values of $\frac{r}{L}$ and t, as long as M has not reached zero, with sufficient approximation

$$i=\frac{1}{L}\frac{dM}{dt}\,t,$$

so that, if M reaches 0 while t is still small,

$$i=-\frac{M_0}{L}$$

will be the final value of the current.

In our experiment the constants were $H_0=400$, $M_0=1.26\times10^6$, $L=10^7$, so that i could rise to 0.126 C.G.S or 1.26 amps. [2] The current can therefore reach the threshold-value 0.8 amp. even with a field of rather more than half the strength assumed in the calculation (cf. one of the experiments in § 4). From the moment at which this value is reached ordinary resistance appears and $\frac{r}{L}$ will be no longer small; the further increase of i above the threshold value i_D follows a different law from below i_D.

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[1] Here is accepted that r is independent of i below the threshold value i_D of i.

[2] The more accurate data given here and at some other places of this translation differ somewhat from those in the Dutch text.

For an accurate calculation of the process above i_D, it would be necessary to take into account the complicated law of increase of the resistance with the current beyond i_D. For our purpose it is sufficiently accurate to assume, that when i_D is exceeded by a small amount the resistance becomes suddenly r' of the order of magnitude above the vanishing point.

In that case, $\frac{dM}{dt}$ remaining the same as before, the current will be able to rise by a small amount $i - i_D = \frac{1}{r'} \frac{dM}{dt}$, which will soon be reached, will then become constant and, on M and $\frac{dM}{dt}$ becoming zero, disappear again in a short time. In view of the value of M and r' we may, if M does not change very rapidly, disregard $i - i_D$, unless we intend an explanation of all the details of the experiment.

We therefore come to the conclusion, that, M_0 being sufficiently large, the current (Fig. 2) on M diminishing to 0 will reach the threshold-value belonging to the temperature of the experiment and after the induction being completed will continue, while only

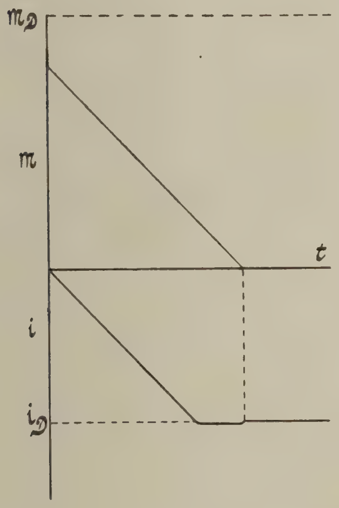

Fig. 2.

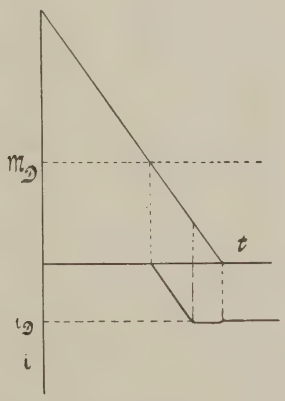

Fig. 3.

after a long time t' according to the relation

$$i' = i_D \, e^{-\frac{r}{L} t'}$$

in accordance with the large value of the time of relaxation $\frac{L}{r}$ an appreciable diminution of i will be observed.

The case, that the initial value of M is above the threshold-value of the production of resistance M_D, is represented in Fig. 3, which after the foregoing needs no special elucidation. The result is apparently again dependent on the threshold-value of the current (see also one of the experiments in § 4).

As appears from the values given above an initial field much smaller than M_D was sufficient in our experiment.

According to the above calculation it was to be expected, that the examination of the magnetic action of the coil could be performed with a simple compass-needle brought near the cryostat.

§ 4. *Details of the observations.* The result proved the correctness of the discussion contained in the previous sections. The field was taken at 400 gauss. In 10 seconds it was reduced to 200 gauss and immediately afterwards the electromagnet was rolled away in 5 seconds. The compass-needle which was then placed beside the cryostat to the East of it on a level with the coil and at a distance from it of 8 cms pointed almost at right angles ¹) to the meridian. When the action on the magnet was compensated by means of a second coil placed on the other side (West) of it of about the same dimensions as the experimental coil and of 800 turns, it was found that the coil was carrying a current of about 0.6 amp. ²). This was further confirmed by turning the coil and by moving the compass-needle to various positions about the cryostat ³). During an hour the current was observed

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¹) The field of the earth being distorted by machinery the action of the latter was compensated by magnets and there resulted a weaker field (note added in the translation).

²) [Calculated from the moment, comp. Comm. N⁰. 140*d* § 8 end. Added in the translation]. The coil has a magnetic moment of 180 and behaves as if the lead possessed remanent magnetisation of some 200 C. G. S. units

³) On repeating the experiment at 4.°25 K. nearly 0.5 amp. was obtained; a later experiment with larger initial field at 2°.3 K. gave 0.7 amp. (see further down).

not to decrease perceptibly (as far as could be judged by the deviation of the needle with an accuracy of 10 $^0/_0$). During the last half hour the coil was no longer at 1.°8 K but at 4.°25 K the temperature of helium boiling under normal atmospheric pressure. Undoubtedly even at this temperature the observation might have been continued much longer without much diminution of the current. A coil cooled in liquid helium and provided with current at Leyden, might, if kept immersed in liquid helium, be conveyed to a considerable distance and there be used to demonstrate the permanent magnetic action of a super-conductor carrying a current. I should have liked to show the phenomenon in this meeting (Kon. Ac. Amsterdam), in the same way as I brought liquid hydrogen here in 1906, but the appliances at my disposal donot yet allow the transportation of liquid helium.

Whereas the experiment, so far as described, shows, that a current when started in a supra-conducting wire continues to flow, the process is immediately stopped as soon as ordinary resistance is generated in the circuit. When the coil is lifted out of the helium, the current is instantaneously destroyed. The temperature of the coil is thereby very quickly raised above the vanishing point of lead (6° K) and the very long relaxation-time is replaced by a very short one. Reimmersion of the coil, if not too soon after the lifting out, does not again produce magnetic action.

If the experiment is made with the windings of the coil parallel to the field, no effect¹) is to be expected. This expectation was in so far confirmed as only a slight effect was observed: this effect can be sufficiently explained by assuming that the attempt to place the windings exactly parallel to the field had not succeeded ²).

If the initial value of the field is higher than the threshold-value, M_D, the result is the same. This case is represented in fig. 3 In one experiment the initial field was 5000 gauss and the

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¹) Nearer consideration points to a small effect, comp. Comm. N⁰. 140*c*. (Note added in the translation).

²) This experiment had been made some days before the main experiment, although it had not been the intention to make it with that position of the coil. At the moment of making this first communication it had not been repeated. [It has been repeated since; again a rest was found. (Note added in the translation. Comp. Comm. N⁰. 140*c*)].

observed magnetic moment corresponded to a current $i = 0.7$ amp.

If the field through the supraconducting coil is first put on and subsequently put off again by bringing the excited electromagnet to its position at the cryostat and then removing it, according to the above reasoning (disregarding the exceedingly slow diminution with the time) no resultant current ought to remain, if no account had to be taken of the threshold-value of the current. Indeed for the second period the relation

$$i - i_1 e^{-\frac{r}{L}t'} = \frac{M_1 - M}{L}$$

holds, if i_1 is the current obtained in the first period during the generation of M_1. This case will be realized, if care is taken, that the threshold-value of the current is not exceeded. It is represented in fig. 4 by the lines which give the field M_b and the current i_b as functions of the time. If during the increase of M the threshold-current is reached, the current will not grow appreciably on further rise of M; from the moment, that the increase of M stops, the current assumes the threshold-value and stays there, until M begins to decrease: it then begins to fall and becomes zero, before the field has disappeared; on the further diminution of the field, the current assumes the opposite sign and the resultant current will be that

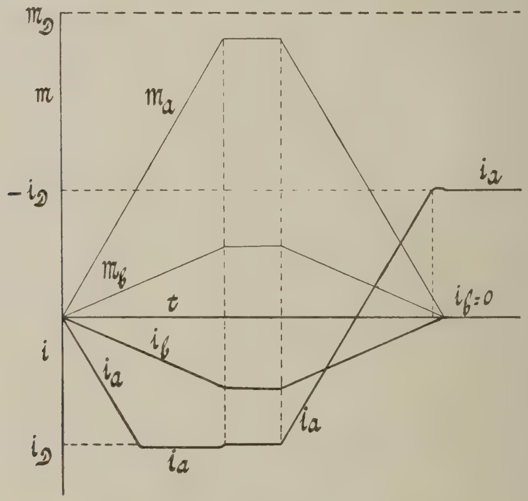

Fig. 4.

which has been formed at the moment that $M = 0$, if it remains below the threshold-value, or the threshold-current itself, if that is reached before M has disappeared. In the latter case the current will exceed the threshold-value by a very small amount from the moment, that the threshold-value is reached, until $M = 0$. In fig. 4 this case is represented by the lines which give the relation between the field M_a and the current i_a.

An instance of the case represented by a is given by an experiment, in which the field brought to the cryostat was 400 gauss. A strong resultant current was observed as in the case, when the coil was first free of current in the field of 400, was then made supraconductive and was finally charged with current by the removal of the field. An instance approximately corresponding to case b was obtained, when the same experiment as a was carried out with a field of 190 gauss. Even in this case the compensation was not quite complete and a little more favourable, when the field was made to approach slowly than with a rapid approach.

With a rising field account has to be taken also of the complication arising out of the influence of the field of the current itself on the threshold-values of field and current. In fact this was not the only feature in the experiments which could not be fully explained yet: naturally as they were performed for the first time, the arrangements were still imperfect [1]). Taken together however they may be said to confirm the main experiment which shows that it is possible in a conductor without electromotive force or leads from outside [2]) to maintain a current permanently and thus approximately to imitate a permanent magnet or better a molecular current as imagined by AMPÈRE.

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[1]) One of the first questions still to be answered is, what part a possible magnetisation of lead or brass may have played in the phenomena: so far no proof has been given, that this may be neglected. However, even now from the experiment, in which the windings were parallel to the lines of force, we may draw the conclusion, in view of the small amount of the action in that case, that the magnetisation of the material of the coil can only play a subordinate part compared to the electromagnetism of the current, to which I have above ascribed the deviation of the compass-needle.

[2]) It may be mentioned here, that it will be possible, by a change of temperature of a small part of the conductor, to insert a resistance in the circuit which can be very delicately regulated without touching it.

The electrons once set in motion in the conductor continue their course practically undisturbed, the electrokinetic energy, represented by MAXWELL by the mechanism of the rotating masses coupled to the current, retains its value, the rotating fly-wheels go on with their velocities unchanged, as long as no other than supraconductors come into play: the application of a small ordinary resistance however stops the mechanism instantaneously. Although the experiment mainly confirmed my deductions as to what had to be expected, a deep impression is made by the very striking realisation which it gives of the mechanism imagined by MAXWELL completed by the conception of electrons.

It is obvious that the subject will lead to further discussions ¹) and plans, but in this paper I may be allowed to confine myself to the simple description of the experiment carried out.

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¹) Compare also MAXWELL, Electricity and Magnetism II, Ch. VI.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 140^c.

H. KAMERLINGH ONNES. Further experiments with liquid helium. J. The imitation of an AMPÈRE molecular current or of a permanent magnet by means of a supra-conductor. (cont.)

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **30 Mei 1914**, p. 167—172).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES. *Further experiments with liquid helium. J. The imitation of an* AMPÈRE *molecular current or a permanent magnet by means of a supra-conductor. (cont.).*

§ 5. *The main experiment repeated.* Although the original experiments on the persistence of a current which is started in a closed supra-conductor have established the fact that the diminution of the current with the time is very small (at least if it is assumed that in the phenomena hitherto unknown magnetic properties donot play an important part), still for the magnitude of the change only an upper limit could be fixed. As no change of the current was observed, this upper limit was determined by the uncertainty in the measurement of the current. The only fact established so far was that, if the change had been greater than 10 °/₀, it would have been observed.

In repeating the experiment it was attempted to determine the change itself or otherwise to reduce its upper limit, in so far as the conditions under which the experiment had to be made allowed this. The same supra-conducting lead-coil was used. As before the current was produced in the closed conductor by induction in order that the circuit might be kept free from connections other than of lead fused together [1]). The current was again measured by compensating the action of the coil on a compass-needle by means of a current in a subsidiary coil. The arrangement was however improved by this coil (of insulated copper wire) being placed in a small vessel with liquid air in a fixed position with respect to the needle. When the compensation was obtained, the experimental coil was turned 180° about a vertical axis and again compensated with the current in the second coil reversed, the magnetic moment of the experimental coil being deduced from the mean of the two observations.

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[1]) An attempt is at present being made to manufacture a supra-conducting current-key.

If the diminution of the current can actually be calculated from the residual micro-resistance given in Comm. N⁰. 133, viz. $\frac{r_{1.°8\,\mathrm{K.}}}{r_{290°\,\mathrm{K.}}} = 0.5 \times 10^{-10}$ or with $r_{290°\,\mathrm{K.}} = 734\ \Omega$ [1]) : $r_{1.°8\,\mathrm{K.}} = 37$, the time of relaxation, with $L = 10^7$, would come to about 270000 seconds or 75 hours. In that case the current would fall by 4 % in three hours. It was hoped that it would be possible with the improved arrangement to establish a diminution of that amount.

The experiment was made with a field of 189 gauss at a temperature of 1.°7 K. The current amounted to about 0.4 amp. (as before no account was taken of the possibility of magnetisation or of induced circulating currents inside the supraconducting material) and during about $2^1/_2$ hours no diminution of the current was observed; it was then necessary to admit a fresh supply of helium into the cryostat: during this operation the temperature rose temporarily to 4.°25 K. During the next hour the current was found to undergo a gradual diminution and to approach asymptotically a new value of about 0.36 amp. which did not show any further change for $1^1/_2$ hours. The observations during the two periods mentioned render it probable, that the change does not attain the value of 4 % in 3 hours as calculated above.

It was considered possible, that the changes of shape of the helium-liquefier and the cryostat during the process of condensation and transfer of the liquid helium, as well as a possible change of zero of the compass-needle which after the magnet has been removed is still near various iron parts of the apparatus, might have had an influence on the values of the current as measured at different moments. Judging by the correspondence of the various readings the accuracy was smaller than had been expected. In again repeating the experiment therefore two compensating coils were used by which compensations on the east and on the west could be effected. They were mounted each in a small vessel with liquid air on a fork-shaped stand and could be rotated about vertical axes in such a manner that the distance of the axes could not change. The same needle served for the compensation on both sides. Guiding pins guaranteed the same position each time of the needle relatively to the compensating coil which was being used. The common support of the two coils was moveable parallel to itself in a horizontal direction on a slide and by means of marks it was possible to place it each time in the same direction and the same position relatively to the vertical axis of the experimental coil. The axes of the three coils were provided with horizontal divided circles moving along fixed pointers. Each measurement consisted of 8 readings in the obvious combinations of 4 positions both with compensation on the left and on the right.

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[1]) This value given already in Comm. N⁰. 140*b* is a more accurate value than that given in Comm. N⁰. 133.

In the experiment with this improved method of reading care was also taken, that the current did not rise above the value at which no further change had been observed at 4.°25 K. The current was therefore raised to only 0.22 amp. (approximate value calculated as before from the observed magnetic moment of the coil), so that the supply of a fresh quantity of helium would probably not have the disturbing effect which had been noticed in the previous experiment. The temperature used was 2° K. In the beginning again a fall of current was noticed which must however be considered as uncertain, inter alia owing to the possibility of the changes of shape of the apparatus and the change of zero of the needle not having been sufficiently eliminated yet in these observations. In the three hours subsequent to the initial period no further diminution was observed, the last observation even giving a small increase. Still in this experiment the accuracy could not be considered greater than about 2% of the measured moment and, as it was found impossible to continue the experiment beyond three hours, again only an upper limit for the change could be established, to be put at about $^2/_3$ % for current and induced magnetisation combined. Taking all the experiments together it may be considered as probable, that the change of the current is less than 1 % per hour which raises the time of relaxation to above 4 days.

§ 6. *Upper limit of the residual micro-resistance according to these experiments.* So far no contradiction has arisen in reasoning on the assumption of the existence of a residual micro-resistance which below the threshold-value of the current again obeys Ohm's law. On this view the upper limit of this micro-resistance for lead, which in Comm. N°. 133 was placed at $0{,}5\,.10^{-10}$ of the ordinary resistance at 0°, can now on the basis of the above observations be moved further back to about $0{,}3\ 10^{-10}$ or $0{,}2\,.10^{-10}$ of the resistance at the ordinary temperature.

§ 7. *Some of the controll-experiments repeated.* In the previous paper a few other experiments beside the main experiment were described: some of these have now also been repeated.

Again we did not succeed to conduct the experiment in which the windings are placed parallel to the field, the coil cooled below the vanishing-point while in the field and then the field removed in such a manner, that the compass-needle, when brought near the cryostat after removal of the electro-magnet, did not show any deflection. After the action of a field of 400 gauss at 4°.25 K. a current of 0.1 amp was found in the coil. This would give 0.045 amp. with a field of 189 gauss, the same as used with the other experiments, whereas the main experiment at the same temperature and inducing field had given 0.4 amp.

More satisfactory was the experiment in which first a current is produced in the coil — analogous to the currents in resistance-free paths as imagined by Weber for the explanation of diamagnetism — and then destroyed by the removal of the field: an almost complete compensation was obtained in this case. The experiment was made with a field of 189 gauss. This result is of special importance as it practically disposes of the supposition mentioned in the previous paper as possible, although very improbable, that magnetic properties of the material of the coil might play an important part in the phenomena.

The current in the coil changes with any new magnetic field applied and with any further change in it, or with any change of position relatively to the field. In this respect the influence of the earth-field may be noted. The current in the coil, when placed with its windings at right angles to the meridian, will assume a slightly smaller value in the one position North-South and a somewhat larger value in the opposite position South-North than in the position East-West which is practically the position in which the experiments were made. In our experiments this action was however too small to be taken into account considering the accuracy which could be attained at the most.

It may be observed that our conductor carrying its current in the absence of an electromotive force, when undergoing the relatively small action of the field of the earth, is analogous to the AMPÈRE molecular currents (in the form of circulating electrons) which play a part in LANGEVIN's theory of magnetism, when they experience a diamagnetic action on being brought into a field, in accordance with LORENTZ's theory of the ZEEMAN-effect

§ 8. *The experiments repeated with the circuit open.*

So far it has been constantly assumed, that the magnetic properties of the material of the coil play but a secondary part in the phenomena observed, when the experiments were arranged so as to produce a permanent current. This view was based firstly on the difference in the results with the windings parallel and perpendicular to the field during the cooling in the field and secondly on the compensation found on applying and removing the field after the conductor had already been cooled to helium-temperature. Furthermore that the part of the effect which is independent of the circulating current must be ascribed to the lead itself, was to be inferred from the fact, that the current is quenched, as soon as the temperature of the coil rises somewhat above the boiling point of helium and passes the point which, as being the vanishing point for lead, has a special physical meaning for this substance.

In order to obtain further information as to the part of the phenomenon which depends upon the material itself, the experiments were repeated after the lead-wire connecting the ends of the coil had been cut, so that the circuit was no longer closed (apart from possible short-circuits in the coil).

This time the experiments with the exception of one could only be performed at 4.°25 K: still there does not seem to be any objection to applying the results for the explanation of the irregularities which had been left unexplained in the main experiments, although these had been mostly carried out at a lower temperature.

In all the experiments a certain residual effect remained which was reduced to about one tenth when the windings were parallel instead of at right angles to the field and in the latter case was fairly well independent of the field. The amount of this effect corresponded to a moment which was equivalent to a current of 0.05 or 0.06 amp. in the closed circuit. In one of the experiments, the only one in which the temperature was lower than 4.°25 K., viz. about 3° K., the moment was estimated to be equivalent to as much as 0.07 amp. The effect with the circuit open is thus very much smaller than in the main experiments. The share born in the effect by the frame of the coil and the lead independently of closing the circuit may therefore be put at less than $^1/_5$ of the total effect in the main experiment.

As a check on former experiments the following additional experiments were made with the coil with the lead wire cut.

In the first place at the ordinary temperature after joining up to a ballistic galvanometer the induction was measured arising from putting on or taking off the field with the windings in the position in which they were supposed in the previous experiments to be parallel to the field. The induction was found to be $^1/_{20}$ of the effect in the position at right angles to the field. This observation may contribute to the explanation of the residual effect observed in the experiments in helium in the position with the windings parallel to the field.

In the second place a known current was sent through the coil and its strength measured by the same method as used in determining the moment of the experimental coil in the experiments with the lead circuit closed. Although the matter requires further elucidation, it would seem to follow from this measurement, that a few of the layers of the coil are short-circuited. After opening the circuit a residual moment remained in the coil as before which was destroyed on raising the temperature slightly above that of the helium-bath.

COMMUNICATIONS

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BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 140^{d}.

H. KAMERLINGH ONNES. Further experiments with liquid helium. K. Appearance of beginning paramagnetic saturation.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **30 Mei 1914**, p. 172—175).

EDUARD IJDO. — PRINTER — LEIDEN.

H. KAMERLINGH ONNES. *Further experiments with liquid helium. K. Appearance of beginning paramagnetic saturation.*

The question, whether paramagnetic substances would show a saturation-effect at high field-strengths, has always been considered a very important one. Although it could hardly be assumed, that the susceptibility would remain independent of the field at higher strengths than were attainable, still so far at the highest fields available it appeared to be the case. LANGEVIN's theory brought the explanation, why so far all attempts to find paramagnetic saturation-effects had remained unsuccessful. According to this theory the magnetisation appears to be determined by the expression $a = \frac{\sigma_m H}{RT}$ where σ_m is the magnetic moment of the molecules per gramme-molecule, R the gas-constant, T the absolute temperature and H the field. As long as a remains below 0.75, the changes of the susceptibility with the field escape the ordinary method of observation and at the ordinary temperature even a substance as strongly paramagnetic as oxygen gives for a with a field of 100000 not more than about 0.05. As I pointed out at the 2nd International Congress of Refrigeration at Vienna (1910) this theory shows that lowering the temperature is the means by which the observation of paramagnetic saturation might be attained and that helium-temperatures are the most suitable for the purpose. In fact as the absolute temperatures to which one may descend by means of helium are 70 and even 150 times lower than the normal temperature, the result will be equivalent to raising the magnetic field at which the observation is made 70 or 150 fold.

I have lately at last been able [1]) to fulfil my desire to attack by this method the problem of paramagnetic saturation which is also fundamental to Weiss's theory of ferromagnetism. In the first place it was necessary to have a substance which might be expected to obey Curie's law, which also follows from Langevin's theory, down to helium-temperatures; in the second place the substance must have a high value of σ_{m}. Both properties I hoped to find combined in crystallized gadolinium-sulphate, a quantity of which Professor Urbain some time ago had very kindly put at my disposal.

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[1]) Viz. by the acquisition a short time ago of an electromagnet (built according to WEISS's principle and utilising his friendly advice) the interferrum of which leaves sufficient room at fields of 20000 for experiments with liquid helium.

Earlier investigations in conjunction with Perrier and Oosterhuis had shown, that gadolinium-sulphate follows Curie's law down to the freezing point of hydrogen and does not show any sign of saturation, which as Langevin's theory shows, if it existed at that temperature, would be ferromagnetic in its nature, as paramagnetic saturation at the value of a which could be reached would not yet be clearly observable. The number of magnetons calculated according to Weiss is large (38). That gadolinium-sulphate would still obey Curie's law at helium-temperatures I felt justified to infer from the fact, that it is a "diluted" paramagnetic substance. The gadolinium-atoms, separated as they are e. g. by the water of crystallisation, are at great distances from each other, and this Dr. Oosterhuis and I in Comm. N°. 139*e* found a favourable circumstance to Curie's law being valid down to very low temperatures.

The experiments have given a confirmation of Langevin's theory which is at least qualitatively even now complete. Before an opinion can be formed as to the quantitative agreement various corrections will first have to be investigated. The most important of these which must not be neglected, especially when the validity of Curie's law is to be tested, is the demagnetising action of the paramagnetisation itself, as the latter attains exceptionally high values. As an instance I may mention that with 0.345 gram of gadolinium-sulphate at 2° K in a field of 15 kilogauss there was observed an attraction amounting to over 100 grammes. Another circumstance that one should keep in mind is that the object of observation consists of small crystals packed on each other.

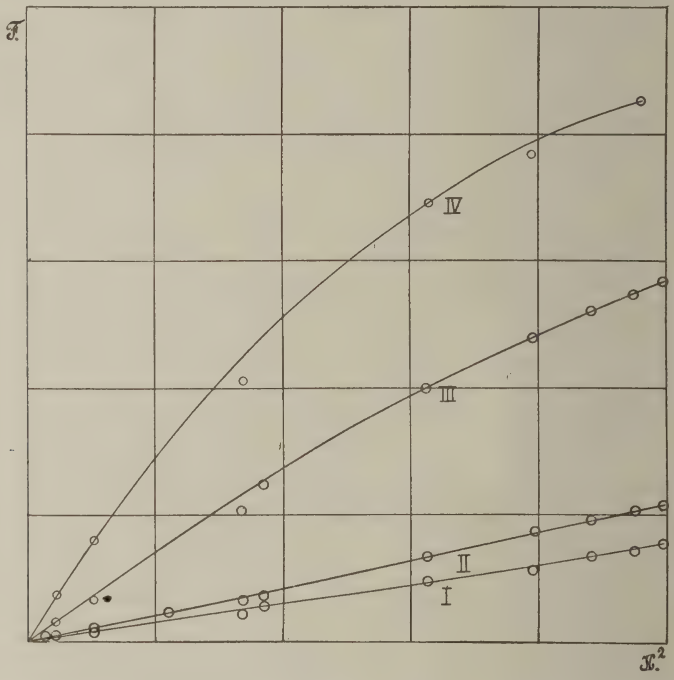
The measurements consisted in determining the attraction in a non-homogeneous field, the gadolinium-sulphate in the cryostat being cooled first in liquid hydrogen under normal pressure, next in hydrogen under reduced pressure, next in helium boiling at ordinary pressure and finally in helium under 4 mms, the apparatus and the fields being the same each time.

The measurements at the boiling point of hydrogen (20.°3 K) had the object to obtain the force at a given point for a given strength of field for controlling the values derived from ballistic calibrations. I hope to return to the details of the measurements and the arrangement of the apparatus afterwards, when an accurate quantitative comparison of the results with LANGEVIN's theory will have been made. It is as yet impossible to decide, in how far deviations are present which might be attributed to the existence of a small zero-point energy which would manifest itself in the manner in which the saturation changes, as well as in a deviation from CURIE's law at weak fields. It seems, however, that these deviations are not sufficiently large to disturb the general aspect.

On this occasion I wish to confine myself to communicating the general aspect of the results as laid down in the adjoining graphic representation on which the experimental numbers may also be read with sufficient accuracy. The curves represent the observed attractive force as a function of the square of the field on the axis between the poles. This field was read as a function of the current from a calibration curve.

Curve I refers to 20.°3 K, curve II to 14.°7 K, III to 4.°25 K and IV to 1.°9 K. Each division along the horizontal axis corresponds to about 90 kilogauss^2, along the vertical axis to 25 grammes. The ratio of the force to the square of the field on the axis of the poles per unit of susceptibility was about $^1/_8$, neglecting small changes in the topography of the field.

If the susceptibility does not depend on the field and its topography remains the same, the curves are straight lines. The small deviations from the straight line at 20.°3 K are probably chiefly due to errors in the topography of the field, seeing that according to earlier more accurate determinations we had to await within the limits of the experiments a susceptibility independent of the field and therefore in this graph a straight line. By means of the deviations from the straight line at 20.°3 K the curves for the other temperatures have been provisionally corrected. It will be seen that for a given field these curves are the more strongly curved the lower the temperature to which one descends, in accordance with Langevin's theory. Within the limits of accuracy to be expected in connection with the neglection of the various corrections referred to above the tangents of the angles of elevation of the tangents to the curves at the origin appear to be inversely proportional to the temperature as required by Curie's law and the deviations of the curves from the tangents as expressed by the ratio between the ordinates of both for a given abscissa are strikingly similar to the deviations of Langevin's curve for the magnetisation as a function of the field expressed in the same manner. The nature of paramagnetic magnetisation is very clearly revealed in these measurements at helium-temperatures.



Errata and addendum Communication N⁰. 141.

p. 4 line 6 from the bottom: for „1/100°” read „1/100th of a degree”.

p. 5 „ 13 „ „ „ for „0,0036628” read „0,0036629”.

p. 10 „ 11 „ „ top after „*thermometers*” add a note: „cf. also Comm. N⁰. 152*c* p. 26 note 3”.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 141^a.

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H. KAMERLINGH ONNES and G. HOLST. On the measurement of very low temperatures. XXIV. The hydrogen and helium thermometers of constant volume, down to the freezing-point of hydrogen, compared with each other, and with the platinum-resistance thermometer.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **30 Mei 1914**, p. 175—182).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and G. HOLST. *On the measurement of very low temperatures.* XXIV. *The hydrogen and helium thermometers of constant volume, down to the freezing-point of hydrogen, compared with each other, and with the platinum-resistance thermometer.*

§ 1. *Introduction.* The measurements which this paper deals with bring the investigations undertaken in Leiden for the purpose of establishing the scale of the absolute temperatures as far down as the freezing point of hydrogen, to a conclusion, in so far that a direct comparison has now been made between the helium and hydrogen scales, by measurements with a differential thermometer, which had the object to test the corrections to the absolute scale of temperatures below 0° C., obtained separately for the helium scale (in XIX of this series) and the hydrogen scale (partially given in XVIII of this series [1])). For the place which the mutual control of these corrections occupies in the more general investigation of the measurement of low temperatures which is being carried out in Leiden, we refer to § 6 Suppl. N⁰. 34*a*. The test could be extended as far as the freezing point of hydrogen, after the compressibility of hydrogen vapour had been determined by KAMERLINGH ONNES and DE HAAS, Comm. N⁰ 127*c*. (June 1912) [2]). Our comparison of the helium scale with the hydrogen scale[1]) by means of the differential thermometer to which was added a new calibration of the Leiden standard platinum thermometer Pt_I' (formerly Pt_I) shows that a very satisfactory agreement has been attained in the temperature determinations.

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[1]) Compare also H. KAMERLINGH ONNES, C. BRAAK and J. CLAY, Comm. N⁰. 101*a*. (Nov. 1907) § 1 under 4*b*.

[2]) In this Comm. a difference was discussed which existed between the temperature determination with a hydrogen thermometer according to the resistance thermometer Pt'_I which was calibrated by means of it and the temperature determination by extrapolation of the isotherms. According to calculations by Dr. KEESOM, suggested by SACKUR's interesting investigation, this deviation might be connected with the theory of quanta (Comp. Suppl. N⁰. 30 and N⁰. 34*a* § 11).

§ 2. *Apparatus.* Two identical thermometers of Jena glass 16^{III}, such as had been formerly used by H. KAMERLINGH ONNES and C. BRAAK, were connected to one manometer. The arrangement was otherwise exactly the same as that used before. The standardmeter was divided into $^1/_5$ m.m. and allowed a direct estimation of $^1/_{50}$ m.m. This gave a considerable saving of time, as it made the use of the measuring eye-piece of the cathetometer unnecessary. The amount of gas in the capillary was measured by an auxiliary capillary of much larger section, as described by CHAPPUIS.

Besides the two thermometer bulbs, the cryostat contained the platinum resistance thermometer Pt_I' and a large pump, which provided for a good circulation of the liquid.

The hydrogen and the helium were purified by distillation, and were both free from other gases.

§ 3. *Calculations.* The temperature for each of the thermometers forming the differential thermometer was calculated from the formula given in Comm. N°. 95*e*, but with a few alterations. The expansion of the glass $f(t)$ of the bulb was not calculated from the quadratic formula given there, but taken from a graphic representation in which the curve was drawn through the points experimentally determined and extrapolated by means of the expansion for a different kind of glass as determined by CH. LINDEMANN. The influence of the different temperature function for the expansion of the glass is about $^1/_{100}{}^\circ$ at hydrogen temperatures, at all other temperatures it is negligible. Moreover the volume was divided into three parts. *a*. The bulb at the temperature t of the bath. *b*. The capillary in which the mean density of the gas was determined, by means of the auxiliary capillary: the mean density is proportional to $\frac{h_0}{h}$, h_0 being the pressure in the auxiliary capillary at 0°, h the measured pressure. *c*. The steel capillary and the volume about the point, the temperature of which is the same as that of the room.

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[1]) The comparison of the hydrogen and helium thermometers by TRAVERS, SENTER and JAQUEROD, Phil. Trans. A 200 (1903), p. 105, has been discussed in Comm. N°. 102. In general their results are in good agreement with our measurements.

If we divide all the members of the above mentioned equation by the volume of the bulb it becomes

$$\frac{H_t}{1+\alpha t}\left[1+f(t)+\frac{\beta}{V_0}+\frac{V_{cap}}{V_0}(1+\alpha t)\frac{h_0}{h}+\frac{V_{dead\ vol.}}{V_0}(1+\alpha t)\,\frac{273}{1+\alpha t_k}\right]=$$

$$=H_0\left[1+\frac{\beta}{V_0}+\frac{V_{cap}}{V_0}\,\frac{h_0}{h}+\frac{V_{dead\ vol.}}{V_0}\,\frac{273}{1+\alpha t_k}\right].$$

The provisional temperature, which is needed for the calculation of the various corrections, was calculated from the resistance of Pt_I'. Even $\frac{H_t}{H_0}$ gives this temperature with sufficient accuracy. The zero-pressure for the hydrogen thermometer was $H_0 = 1191$ m.m. 1), for the helium thermometer $H_0 = 1124$ m m. Circumstances unnecessary to be mentioned here, had prevented these pressures from being made more equal. A new set of determinations in which this will be attended to is planned. The pressure coefficient of hydrogen at the above mentioned pressure was taken at 0.0036628; for helium at 0.0036614, the value derived by KAMERLINGH ONNES 2) from the isothermals at 0° C. and 100° C. If we calculate with the pressure coefficient 0.0036617 deduced from the isothermals of 20° C. and 100° C. we find, after

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1) At these pressures even at the melting-point of hydrogen no attention need be paid to the thermo-molecular pressure according to KNUDSEN (Comp. Suppl. N⁰. 34 § 7 and a Comm. by H. KAMERLINGH ONNES and S. WEBER which is shortly to be expected, on the determination of the temperatures which can be obtained with liquid helium).

2) H. KAMERLINGH ONNES, Comm. N⁰. 102*b*. The value is here increased by 0.0000001, in consideration of the value 273.09 since assumed for $T_{0^\circ C}$. Comp. H. KAMERLINGH ONNES and W. H. KEESOM. Die Zustandsgleichung. Math. Enc. V 10, Suppl. N⁰. 23, Einheiten *c*, and § 82*b*.

the introduction of the necessary corrections, almost the same temperature on the absolute scale.

§ 4. *Arrangement for the resistance measurement.* In order to measure and to compare resistance thermometers two identical differential galvanometer circuits were fitted up according to KOHLRAUSCH's method. Both galvanometers can be read from one place, so that nearly simultaneous measurements can be made. This removes all irregularity in the temperature of the bath in the comparison of resistance thermometers. Two moving coil differential galvanometers from HARTMANN and BRAUN were used. With an additional resistance of ± 1000 Ω in each of the coils these are practically aperiodic in the measurement of resistances less than 130 Ω, as with all our other thermometers. The sensitivity is sufficient to measure $\frac{1}{10000}$ Ω with a current of ± 5 milliampères, while the condition of proportionality between deflection and current-strength is very well fulfilled.

Test-measurements have shown, that with this arrangement resistances of about 100 Ω, such as our thermometers have at ordinary temperature, can be compared to $\frac{1}{100000}$ without any difficulty. Our experience with moving coil differential galvanometers, for this purpose at any rate is very favourable [1]).

In the manner described we attained a much greater rapidity of measurement than was possible by the method described in the previous papers of this series, and this in its turn increases the accuracy.

We must also refer to our experience with thermometers in which the wire was sealed to the glass (Comm. N°. 95*b* § 1). For temperatures above that of liquid air they are not unsuitable, although even here they are less constant than those with a free thread. After immersion in liquid hydrogen their resistance was found to have increased by about one tenth of an Ohm. Each further immersion in hydrogen carried with it a permanent change of resistance, so that we replaced these thermometers by other ones with free threads wound on porcelain tubes with a double screw thread baked in. After a thermal treatment, consisting in several immersions in liquid hydrogen followed by moderate heating these became satisfactorily constant.

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[1]) Compare JAEGER, Zeitschrift f. Instrumentenkunde 1904.

§ 5. *Results.* In the following table the results of our researches

TABLE I.

	t_{H_2}	t_{He}	θ_{H_2}	θ_{He}	$W_{Pt'I}$
	0				135.450
1	— 23.96	— 23.94	— 23.96	— 23.94	122.613
2	43.09	43.07	43.09	43.07	112.278
3	61.50	61.49	61.50	61.49	102.280
4	79.57	79.51	79.57	79.51	92.422
5	102.72	102.69	102.70	102.69	79.674
6	113.58	113.55	113.56	113.55	73.629
7	130.46	130.41	130.43	130.41	64.189
8	182.88	182.81	182.82	182.79	34.180
9	186.79	186.70	186.73	186.68	31.904
10	195.24	195.15	195.18	195.13	26.988
11	204.79	204.69	204.71	204.67	21.491
12	212.61	212.52	212.52	212.50	17.097
13	216.25	216.15	216.16	216.13	15.119
14	252.80	252.68	252.66	252.64	1.924
15	256.23	256.10	256.08	256.06	1.601
16	258.56	258.41	258.39	258.37	1.453
17	252.80		252.66		1.925
18	253.78		253.64		1.819
19	255.20		255.05		1.685
20	257.22		257.05		1.531

are found. The two first columns contain the hydrogen and helium temperatures calculated from the formula given above. Column

3 and 4 contain the corrected temperatures on the absolute scale deduced from the hydrogen and from the helium thermometer, column 5 contains the resistance of the platinum thermometer Pt_I'.

The agreement is on the whole very satisfactory.

We have already mentioned that with thermometers of the kind described an accuracy of about $^1/_{50}{}^{\text{th}}$ of a degree might be expected. Our measurements show this to be the case; only in a few points larger deviations occur. These can readily be explained by a small defect which will be avoided when repeating the experiments, namely that the cryostat which had to be used was not quite symmetrically built. When both auxiliary capillaries worked properly this was not of much consequence. But (except fortunately in the for us most important determinations viz. at the hydrogen-temperatures) the helium capillary got out of order, so that the distribution of the temperature of the stem of the helium thermometer had to be deduced from the observations with the hydrogen capillary. This circumstance has the greatest influence at temperatures at which the methyl chloride and the oxygen evaporated under reduced pressure, and it is exactly there that the greatest deviations occur.

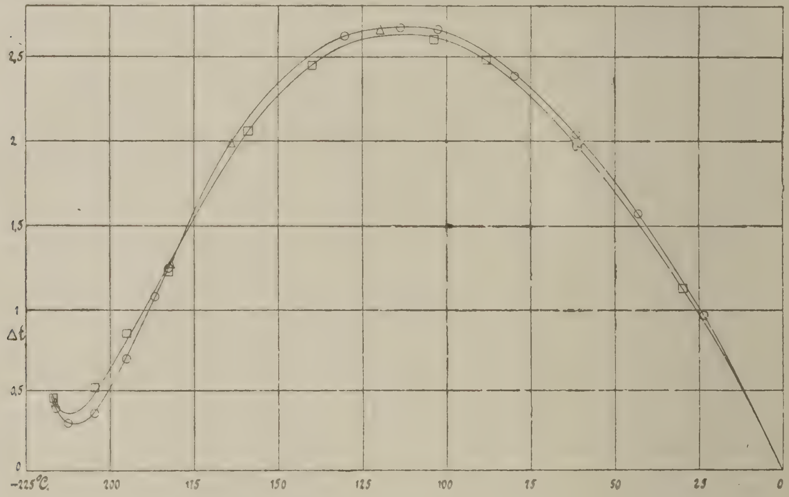

Fig. 1.

The readings of Pt'_I allow a comparison with the measurements of 1906—1907.

In Fig. 1 the deviations from the linear formula $t = -243 + 243\,\frac{W}{W_0}$ are represented for all three calibrations, at temperatures above — 217° C. The circles refer to the calibration of 1913, the triangles to 1907 and the squares to 1906. For the calculation of temperatures in this field the above formula with the deviation curve belonging to it has been recently used in the Leiden-researches.

The differences between the calibrations of 1913 and 1907 are less than $^1/_{50}$th of a degree throughout. The fact that the differences with the first calibration (1906) are more considerable must undoubtedly be attributed to the mechanical treatment of the wire: after the first calibration the wire broke, and had to be re-wound. It must be ascribed to chance, that the deviations are so small just at the points of the second calibration.

§ 6. *The field of utility of the platinum resistance thermometer at low temperatures. Resistance thermometers for other fields of temperatures.* The curve in fig. 1 shows at once the peculiar behaviour of platinum below — 200° C. At this temperature a change of direction in the line which gives the resistance as a function of the temperature is sharply marked. In fig. 2 the deviations from the formula given above in the oxygen field are once more represented (circles) and also those for the thermometers Pt_i (squares) and Pt_g (triangles), which were also directly compared with the hydrogen-thermometer by Dr. C. Dorsman and us. It is clear from the curves, that we have to deal with a specific peculiarity of platinum, which makes it very unsuitable to be used as a thermometer in this field, as accurate interpolations are impossible. For this reason in the field of temperatures below — 200° C. a gold

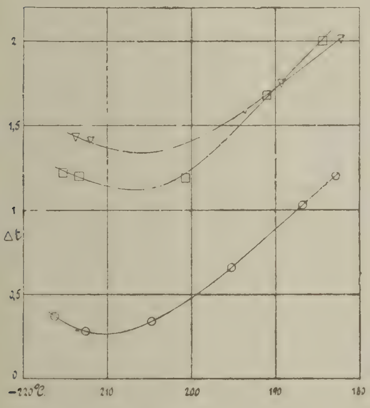

Fig. 2.

thermometer is preferable to a platinum one, as has already been pointed out by KAMERLINGH ONNES and CLAY [1]).

At hydrogen temperatures both platinum and gold are no longer approximately linear. Here and at helium temperatures manganin and constantin proved to be nearly linear and fit for resistance thermometers. Concerning these we refer to a future comm. dealing with resistance measurements in particular for the determination of the specific heat of mercury at helium temperatures.

§ 7. *Comparison of our thermometer Pt'_I with other platinum resistance thermometers.* Comparing our measurements with those of F. HENNING [2]) formulae of the form:

$$\Delta R = M(R-1) + N(R-1)^2 \text{ and } \alpha' = \frac{\alpha^2 N}{c}, \quad M = \frac{\alpha N}{c}(1-100c) - 1$$

were used. This was done because there were objections to a direct determination of the temperature coefficient by measuring the resistance of Pt'_I at 0° C. and 100° C. which since the first calibration had never been brought to a temperature above the ordinary. We found

t	$R=\frac{W}{W_0}$ (K.O. and H.)	$R=\frac{W}{W_0}$ (HENNING)	$10^5 \Delta R$	$R-1$
— 23.96	0.90523	0.90449	74	— 0.09551
— 43.09	0.82893	0.82775	118	— 0.17225
— 61.50	0.75511	0.75340	171	— 0.24660
— 79.57	0.68233	0.67989	244	— 0.32011
— 102.72	0.58822	0.58492	330	— 0.41508
— 113.58	0.54359	0.54007	352	— 0.45993
— 130.46	0.47389	0.46986	403	— 0.53014
— 182.88	0.25234	0.24686	548	— 0.75314
— 186.79	0.23554	0.22998	556	— 0.77002

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[1]) Comm. N°. 95. A gold thermometer has been used also by CROMMELIN down to — 205 °C., Comm. N°. 140*a*.

[2]) Ann. der Phys. 4te Folge Bd. 40, 1913.

These numbers give: $M = -\ 0.0078758$
$N = -\ 0.0007605.$

And further $c = -\ 0.30.10^{-5}$
$100\alpha' = \quad 0.38821.$

From the results it appears that our platinum thermometer, as regards its constants, lies between the platinum thermometers N⁰. 1 and N⁰. 7 used by HENNING in his investigation. This was to be expected, as these thermometers, like ours, were obtained from HERAEUS, N⁰. 1 and Pt'_I being of earlier date. The difference with the values calculated by HENNING is caused by the fact that his calculation was based on our calibration of 1906 which differs from our present one and that of 1907 (Comp. § 5).

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 141^b.

H. KAMERLINGH ONNES. Further experiments with liquid helium. L. The persistence of currents without electro-motive force in supra-conducting circuits. (*Continuation of J*).

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam,* **27 Juni 1914**, p. 487—493).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES. *Further experiments with liquid helium. L. The persistence of currents without electro-motive force in supra-conducting circuits.* (Continuation of J).

§ 9. *The preservation of an electro-kinetic momentum.* All the phenomena, that were dealt with in the preceding sections (J) [1]) showing the persistence of the magnetic moment of the coil, without the action of an electro-motive force, agree with what was deduced on the supposition, that a current flows through the coil of the value calculated, and which diminishes according to the time of relaxation calculated. At the same time, it was desirable to have a conclusive proof, that the magnetic moment of the coil is really caused by a current. We should then be able to prove conversely by the continuation of the moment, that the time of relaxation of the current is very long, and a value, or otherwise an upper limit could be given for the micro-residual-resistance of the conductor in which this current flows.

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[1]) Disregarding the existence of threshold-values of current and field and considering that, below these, supra-conductors add up algebraically without appreciable loss the inductional impulses which act on them in the course of time, two points of view may be very simply contrasted in connection with the experiments so far described on the production of currents persisting for a long time.

The first is analogous to that taken up in Weber's explanation of diamagnetism. In this case we deal with supra-conducting circuits which are currentless outside the magnetic field. By bringing these into a field currents may be obtained which persist as long as the field remains unchanged. But when the field disappears the circuits become again free of current. In this manner a good imitation is obtained of diamagnetic polarisation. The other point of view may be called the antilogon of that of Weber. We provide in a magnetic field supra-conducting circuits which are free of current. When these circuits are brought outside the field, they show a current persisting for a long time. Outside the field they imitate permanent magnets. It must, however, not be lost sight of, that this imitation is in so far incomplete as, when the circuits are brought back into the field, they return to the currentless condition.

I got this proof in the following manner.

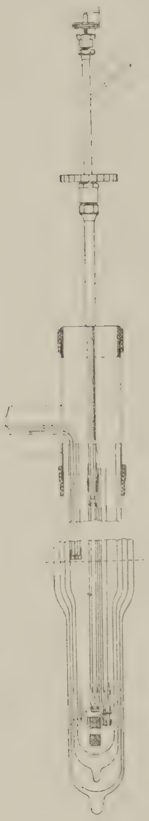

Fig. 1.

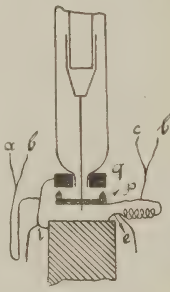

Fig. 2.

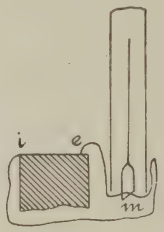

Fig. 3.

On either side of the place, where the ends of the windings of the coil are sealed together and close to it, two wires *b*, *b* (see fig. 2 and 1) were fixed which lead to a ballistic galvanometer. Between these points of attachment the current can be cut through under helium, by pulling up by a thread a bronze loop provided on the inside with a knife edge at *m* (see figs 3 and 1. Figs 1 and 2 give a combined view of the experiments of sections 9 and 11). The thread runs through a tube the lower part of which is of glass and can be moved by means of a rubber-tubing attachment at the top of the apparatus (fig. 1). The coil was cooled to 2°.4 K. in a field of 200 gauss by helium evaporating under reduced pressure. The current was again produced through induction by removing the field. When the compass needle with the compensation-coils was arranged, as before, beside the cryostat, a moment corresponding to a current of 0.36 amp. was registered. The observation was continued for an hour, in which the diminution of the current in 45 minutes was within the limits of probable error of the measurement $(2^0/_0)$; after this the circuit of the coil was cut through. The needle of the compass fell back to a deviation that corresponded to a current of 0.05 amp. in the coil. The ballistic galvanometer (with a negligible self-induction and with 2000 Ω in the circuit) showed an electro-kinetic momentum Li of 300000, from which follows with $L = 10^7$, that a current of about 0.3 amp. flowed in the coil. The remaining moment is again the same fraction of the principal effect as was observed previously, it was extinguished as soon as the coil was pulled up above the liquid helium. The experiment proves conclusively, that a current does really flow through the coil.

§ 10. *Further consideration of the momentum produced in the coil, when the circuit is not closed. Persisting* FOUCAULT-*currents.* In the previous experiments the question arose in how far magnetic properties of the frame of the coil, which developed at the lowest temperatures, had an influence, and whether a part of the moment that remained, when the coil, without the ends being connected, was cooled and exposed to the field, was due to windings which were short-circuited. For this purpose first of all a tube of brass, exactly like that used as the frame of the coil, was cooled in the field. It showed no residual magnetism.

To get further light on possible short-circuits in the coil Pb_{XII}, after it had been shown that cooling in liquid air did not alter its moment, a new coil of 650 turns was wound, in which the possibility of short-circuiting was excluded by insulation of the windings by picein and paper. It is true, that the magnetic properties of these materials are not known, but from the extinction of persisting currents immediately above the boiling-point of helium, which was found in the course of the experiments, it is almost certain, that the phenomena are entirely due to the lead. It was ascertained, that this coil was superconductive, which was a welcome result also for the reason, that the wire had been manufactured by compression, and this process gives a much better guarantee of getting the same product again by using the same method, and therefore of obtaining beforehand the certainty of the wires prepared in this way being supra-conducting. In making the experiment with 200 gauss at 2°.4 K, a residual effect of the same order as with Pb_{XII} was found, but smaller. The principal current was 0.5 and the residual current 0.020 Amp. It becomes probable, when these figures are compared with those found with Pb_{XII}, that in the latter there really is some short-circuiting, but there is also apart from the effect due to the short-circuited windings a moment caused by the lead.

It seems as if in the mean time this may be attributed to circular currents in the lead of the wire, which are possible owing to the wire having a certain thickness. We must distinguish in the wire between an inside which is turned towards the axis of the coil, and an outside. In the wire, even when the circuit is opened, a current arises, in which the electricity passes along the whole length of the windings on the outside of the wire (that is not closed in itself), in order to turn round at the one end of the wire and go back along the internal side. With induction in the closed circuit this current is superposed upon the mean electric movement in the circulating current, so that in the wire there is say a stronger current on the outside, and a weaker on the inside. If by means of a galvanic cell a current is sent through the wire, the same phenomenon arises through the action of the field of the current itself. We are here evidently dealing with persisting Foucault-currents [1]).

§ 11. *A supraconducting key.* In the experiments so far described the supra-conducting closing of the conductor tested for supra-conductivity was obtained by melting the two ends together. Now that these experiments had proved, that a current generated in a circuit which is supra-conducting over its whole length continues without electro-motive force, we could investigate in how far an electric contact interposed in an otherwise supra-conducting circuit, measured by the amount of conductivity of supra-conductors, might be considered as having no resistance. The immediate cause of this investigation was a suggestion made by my colleague Kuenen, whether the current the relaxation period of which was to be studied, might not be obtained in the coil by short-circuiting.

I thought then, that the transitional resistance in a contact to be manipulated under liquid helium could hardly be made small enough for this purpose. The transitional resistance of a stopcontact treated with all due care at ordinary temperature is not likely to be less than 0.0001 Ω, which is still 100.000 C. G. S. while the micro-resistance of the coil itself is only 37. It has

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[1]) Several of the well known experiments by Elihu Thomson with alternating currents could also be made with parallel currents and supra-conducting experimental objects.

p. 19 line 11 from the top: after spring insert: connecting two parts of the rod and governed by a wheel.

Errata Communication N⁰. 141*b*.

p. 18 line 2 from the bottom: for parallel read continuous now been found, however, that transitional resistances, such as we are considering can become very small at low temperatures. A quite moderate pressure, between two pieces of lead appeared to be sufficient for the purpose. The arrangement is shown in Fig. 2. The small lead plate *p*, provided with three small cones directed upwards and connected with the coil through a spirally-wound part of the lead wire which acted as a spring, is attached to a thin rod (partly formed of wood) and was pressed against the block soldered to the glass tube by screwing up the rod, the force being accurately regulated by means of a spring (see top of fig. 1). The tube is provided with a number of side-openings to prevent the very much intensified heat convection (caused by resonance phenomena) which occur in tubes closed at the top when the bottom is at a very low temperature, and which would lead to excessive evaporation of the helium.

By means of this simple key we were enabled to arrange the following experiment. To each extremity of the windings of the coil two wires were attached (fig. 1 and 2). By means of the one pair *ac* a current can be sent through the coil. The other pair *bb* can be connected to a ballistic galvanometer. Moreover the two ends are connected to the two parts of the supra-conducting key. With the key and the galvanometer open, a current is sent through the cooled coil, in the neighbourhood of which the compass-needle has been mounted. The coil is then closed in itself which gives no change in the deviation of the needle. One can then convince oneself as long as one likes, that the side-current, which in ordinary cases is immediately extinguished, remains unaltered in the supra-conductor; the galvanometer connection is then closed, which also brings no change in the current, and if thereupon the current connection is opened this is accompanied by a throw of the ballistic galvanometer in the circuit of which the current is instantly extinguished and by a return of the needle of the compass into the position which it would also take up, if the current in the closed coil had been generated by a magnetic field equal to that of the current itself. The continuation of the movements in MAXWELL's mechanism, when it has a supra-conductor as carrier, is demonstrated by this experiment with equal clearness and simplicity.

§ 12. *Combination of parallel currents into one of greater strength.* In trying to make the same experiments with mercury that we have made with lead, it will be necessary in so far to change the experiment, that one winding will be sufficient. This might be got by freezing mercury in a capillary tube returning in itself with an expansion head (like our other U-shaped mercury resistances). The chief questions then are 1) if with a conductor of as large a section (keeping for the present to the circular form) as would be necessary, with a view to the threshold value of current density, in order to get an action comparable to that with the lead coil, the threshold value of current density — of which as in N⁰. 133 it is assumed that it is determined principally by the current density — does not undergo a considerable diminution in consequence of the larger section, as some considerations in N⁰. 133 would make us fear, and 2) if we can reckon with the microresidual resistance as an ordinary resistance even for such a completely different section as that for which it has been determined. An inducement to try the experiment immediately with a lead ring 1) was a remark by my colleague

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1) I am glad to mention here that Mr. J. J. TAUDIN CHABOT of Degerloch (Württemberg) shortly after my paper on the disappearance of resistance in mercury and, as I found afterwards, only acquainted with my result, that the resistance of gold and platinum in an absolutely pure condition would probably disappear altogether at extremely low temperatures, communicated to me a number of suggestions regarding the condition into which metals pass below this temperature and which he would like to be considered as a distinct "fifth" state of aggregation.

Amongst these suggestions was the following: "if a ring (of gold) is brought to the condition of absolutely no resistance (in helium), an impulse (viz. by induction) will be sufficient to produce a permanent current, which will make the ring into a magnetic shell, as long as the temperature of the metal remains below a certain critical value". By critical value was meant — not the vanishing point as discovered afterwards — but the temperature characteristic of each metal at which, according to my earlier views, the resistance of the pure metal would become zero independently of the current-strength. The idea, however, underlying this speculation — which was further developed by supposing the cooled ring to be subjected to a magnetic field that was to be removed afterwards — was also applied in my experiments for the purpose of obtaining persisting currents in supra-conductors, and in the above last experiment actually with a ring as the conducting circuit.

At the time I was so much occupied with the investigation of the peculiar

EHRENFEST, that the experiment could be made equally well with the windings "parallel" as it had been made with the windings in "series." A calculation (by estimation and further proceeding in the same way as with the coil) about the experiment with a lead ring of an internal radius of 1.2 cm., of a thickness of 0.3 cm., and of a width of 0.35 cm. and assuming, that the threshold value found for the thin lead wire would also hold for the thick ring, showed me, that it might succeed very well.

This proved to be the case. The current of 320 amp. that was registered in the ring remained constant for half-an-hour to 1 %, hence the current density of 30 was in this experiment not much smaller than it had been in one of the experiments with the coil of lead wire, viz. 49. This may for the present be regarded as a confirmation of the supposition, that the threshold value of current strength of a conductor is mainly a threshold value of current density for the material of the conductor.

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laws of electric conduction in mercury below the vanishing-point and of the degree to which currents might be realised in resistance-less circuits without electromotive force, that I had not yet attacked nor was able to fully go into the problems relating to currents to be generated in closed supra-conductors by induction (amongst which problems that of the imitation of diamagnetic polarisation was an obvious one). Still Mr. TAUDIN CHABOT's letter was the cause of my coming even then to the conclusion, that in order to be able to obtain persisting currents outside the magnetic field by induction, an artifice based on the peculiarity of supra-conductors was required. As such I then found, that the cooling which is to make the conductor supra-conducting is not proceeded with, until the conductor is in the field which is to be used for the induction. Afterwards it was found, that by utilizing the knowledge of the threshold values of current and field circumstances may be realized, in which a permanent current may be obtained outside the field by induction on a circuit which has been made supra-conducting by cooling before the field is applied.

Erratum Communication N⁰. 142.

In the title of Comm. N⁰. 142*b* omit the word: „gold".

Errata Communication N⁰. 142.

p. 4 line 9 from the bottom: for „49°.88" read „— 38°.93 C."
p. 4 „ 9 „ „ „ „ „25.095 Ω" „ „26.800 Ω".
p. 4 „ 8 „ „ „ „ „115.0 Ω" „ „125.0 Ω".
p. 19 „ 2 „ „ „ „ „abscissa" „ „ordinate".

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 142^a.

H. KAMERLINGH ONNES and G. HOLST. On the electrical resistance of pure metals etc. IX. The resistance of mercury, tin, cadmium, constantin and manganin down to temperatures, obtainable with liquid hydrogen and with liquid helium at its boiling point.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **27 Juni 1914**, p. 506—511).

Vol. XIII. Comm. N°. 142*a*, fig. 1. In the numbers of Δw for 0.05 read 0.50.

H. KAMERLINGH ONNES and G. HOLST. *On the electrical resistance of pure metals etc. IX. The resistance of mercury, tin, cadmium, constantin and manganin down to temperatures, obtainable with liquid hydrogen and with liquid helium at its boiling point.*

§ 1 *The resistance of wires of solid mercury.*

Several mercury resistances were compared with the platinum resistance thermometer Pt_I' of the laboratory, first in liquid oxygen, then at a number of other temperatures, with the differential-galvanometer according to KOHLRAUSCH's method.

T	$W_{obs.}$	$W_{calc.}$	$\triangle W$
< 4.19	supra-conductor		
4.19	0.0560	0.479	0.421
4.27	0.0600	0.489	0.429
4.33	0.0636	0.496	0.432
4.37	0.0656	0.500	0.434
14.57	0.9390	1.667	0.728
15.78	1.069	1.806	0.737
17.89	1.298	2.047	0.749
20.39	1.563	2.333	0.770
80.92	8.086	9.261	1.175
90.13	9.088	10.316	1.228
116.52	12.000	13.337	1.337
122.81	12.694	14.056	1.362
132.72	13.800	15.190	1.390
141.83	14.855	16.233	1.378
154.22	16.354	17.651	1.297
165.80	17.806	18.976	1.170
184.92	20.311	21.164	0.853
218.69	24.716	25.029	0.313
233.53	26.694	26.731	0.037
234.16	26.800	26.800	0.000

The result of these determinations was as shown in the table on p. 3 ($T =$ temperature on the Kelvin scale, with $T_{0°\text{C.}} = 273.°09$).

In the third column are given the values, which would have been obtained, if the resistance diminished linearly from the melting point down to the absolute zero.

$$W_{\text{calc.}} = \frac{T}{T_s} W_s = \frac{T}{234.16} 26.800 = 0.11445\ T.$$

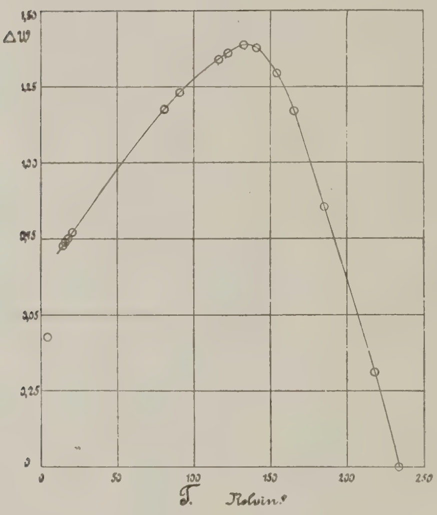

Fig. 1.

Column 4 gives the deviations of the real values of the resistance from those, calculated by means of the linear formula. These deviations are also plotted in the figure. The relation between electrical resistance and temperature seems to be of a very complicated character.

§ 2. *Direct determination of the change in resistance at the melting point.*

Of two resistances, which were frozen without auxiliary bath, the change in resistance in melting was determined directly. The first one consisted of a narrow capillary filled with mercury, section ± 0.0015 mm². At 49°.88 the resistance was 25.095 Ω, immediately above the melting point 115.0 Ω,

$$\text{the ratio } \frac{w_{\text{liq}}}{w_{\text{sol}}} = 4.66.$$

The second capillary had a section of 0.43 mm². With this resistance the ratio 4.50 was found.

As a preliminary value of the melting point — 38°.93 C. was found [1]).

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[1]) Our measurements date of 1912. In the meantime was published the paper of F. Henning, Ann. d. Phys. (4) 43 (1914) p. 282, who finds — 38°.89 C.

§ 3. *Indirect determination of the change in resistance at the melting point.*

During the numerous determinations of mercury resistances in liquid helium (Comm. No. 133), we always measured the resistance at ordinary temperature too. By means of the resistances of solid mercury of § 1 and of the well-known behaviour of liquid mercury, we calculated in each case the ratio $\frac{w_{\text{liq}}}{w_{\text{sol}}}$.

As in these experiments the mercury resistance was suspended in a vacuum-vessel cooled from the outside, the freezing took place very slowly.

We found:

23	May	1911	4.40
30	„	„	4.63
27	Oct.	„	4.41
			4.84
12	Jan.	1912	$4.30 w_{50}$
			$5.06 w_{130}$
17	Febr.	„	4.69
			4.19
22	„	„	4.30
14	June	„	4.37
			4.90

As probably the highest figure thus obtained comes nearest to the true value of the ratio, we will be not far from the truth, if we assume the number 5 for the mean ratio.

This result has also been found by BALTRUSZAJTIS [1]), who obtained 4.90 as highest value in his melting-experiments.

It is remarkable, that the ratio of the change with temperature of solid and liquid mercury is also about 5; the increase of resistance per degree remains thus fairly constant in melting.

§ 4. *Some determinations of the change in resistance with the temperature of metals and alloys.*

a. Object of the experiments. We made a series of determinations, mainly for orientation, about the change of resistance of different metal wires down to helium temperatures. The purpose of those determinations was to find a metal or an alloy, which could be used as a resistance thermometer down to the lowest helium temperatures. The results of the measurements are plotted in figure 2. Of special interest is the behaviour of manganin and constantin. While with copper, tin, iron and cadmium no further change in resistance could be established in the region of the lowest temperatures, it appeared, that the resistance of manganin diminished considerably and in an approximately linear way with the temperature, from the lowest oxygen temperatures down to the region of the helium temperatures. So that wires of manganin might be used equally well as wires of constantin (the suitability of which was shown on a former occasion), as resistance thermometer in this region of temperatures.

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[1]) A. BALTRUSZAJTIS, Cracovie Bull. Akad. Nov. 1912.

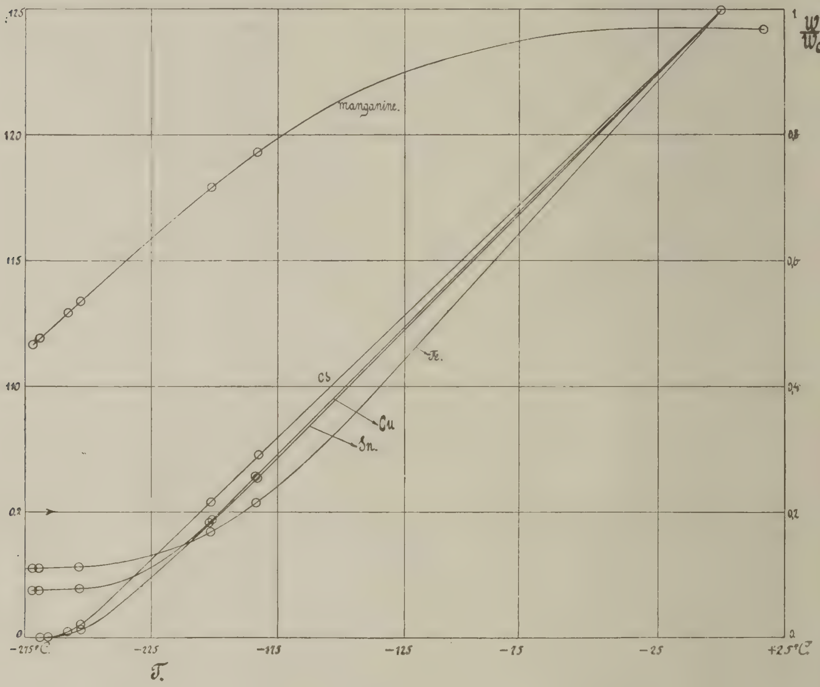

Fig. 2.

b Pure cadmium and pure tin. Pure cadmium (KAHLBAUM) was cast in a glass tube like mercury. From the tin (KAHLBAUM) a thin wire was cut on the lathe.

t	Resistance of tin	t	Resistance of cadmium
16.5	271 $10^{-3}\Omega$	16.6	76.7 $10^{-3}\Omega$
−183.2	66.2	−183.2	20.9
−201.4	46.9	−201.2	15.7
−252.9	2.99	−252.9	1.45
−258.3	1.18	−258.3	0.58
−268.9	0.132	−268.9	0.032

c. Copper and iron. The copper wire was made of commercial electrolytic copper 1). The iron was from Sweden (Kolswa II). It had already been used by Dr. B. BECKMAN for measurements concerning the influence of the magnetic field on the resistance.

t	W_{copper}	W_{iron}
− 183.7	34.5	3.90
− 201.7	24.7	3.05
− 253.5	10.5	2.04
− 269.5	10.0	2.00
− 272.0	10.0	2.00

The resistance approaches here to a definite limiting value, in the same way as this has already been found for other not quite pure metals (Comm N⁰. 119).

d. Constantin and manganin. The temperature coefficient of constantin which is extremely small even down to oxygen tempera-

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1) W. MEISSNER (Verh. D. Phys. Ges. (16), 262, 1914) used much purer copper. In his determinations the resistance at the boiling point of liquid hydrogen was only 0.26 % of the resistance at 0° C.

tures, increases considerably in the region of the hydrogen temperatures, so that constantin wires are suitable thermometers in this region and especially in the region of helium temperatures.

T	$W_{\text{constantin}}$ $Const._{c\,1}$ [1]	$T_{\text{calc.}}$	$T - T_{\text{calc.}}$
90.75	145.680		
65.18	144.320		
20.36	138.259	20.36	0.00
18.98^5	137.988	19.00	—0.01
17.33	137 662	17.37	—0.04
15.83	137 355^5	15.83	0.00
14.32	137.050	14 30	0.02

T_{calc} are the values calculated by means of a linear formula of the form

$$t = a + bw$$

through the points at 20°.36 and 15°.83. The deviation does not amount to more than 0°.04 and shows thus the suitability of con-

θ	W_{manganin} $Mang._1$
16°.5 C	124.20
—183.0	119 35
—201.7	117.90
—253.3	113.42
—258.0	112.91
—269.0	111.92
—271.5	111.71

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[1] Calibrations of other constantin and gold wires will be given in the paper by W. H. KEESOM and H. KAMERLINGH ONNES on specific heats, Comm. No. 143.

stantin wires as thermometers in the hydrogen region, where the platinum-thermometer would require complicated calibrations (comp. Comm. N⁰. 142*c*).

e. Gold. With a view to measurements of specific heats, which will be published before long (Comm. N⁰. 143) and to investigate the suitability of the gold-thermometer in the region of oxygen- and hydrogen-temperatures, we determined the resistance of a gold wire at a great number of temperatures in those regions [1]. The results show, that in the region of the reduced-oxygen temperatures (mainly below — 200° C.) the gold thermometer does not raise the difficulties, which make the platinum thermometer nearly worthless in that region (Comm. N⁰. 141*a* § 6 and fig. 2).

T	Resistance of gold wire Au_{c1}
14°.18 K	0.2910
15.83	0.3037
17.30	0.3190
19.00	0.3412
20.35	0.3621
65.18	2.2901
72.58	2.6763
83.31	3.2312
87.99	3.4710
90.75	3.6110

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[1] Cf. note 1 on p. 8.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 142^b.

* * *

H. KAMERLINGH ONNES and K. HOF. Further experiments with liquid helium. N. HALL-effect and the change of resistance in a magnetic field. X. Measurements on cadmium, graphite, gold, silver, bismuth, lead, tin and nickel, at hydrogen- and helium-temperatures.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam* **27 Juni 1914**, p. 493—501).

Comm. N°. 142*d*, p. 37, line 14 from the top: for 0.3316 cm. read 0.03316 cm.

H. KAMERLINGH ONNES and K. HOF. *Further experiments with liquid helium. N.* HALL*-effect and the change of resistance in a magnetic field. X. Measurements on cadmium, graphite, gold, silver, bismuth, lead, tin and nickel, at hydrogen- and helium-temperatures.*

§ 1. *Method.* The method was the same as that used in the measurements of this series by H. KAMERLINGH ONNES and BECKMAN (cf. Comm. N°. 129*a* and others). The notation is also the same as in the previous papers. As regards the HALL-effect, we used both the method in which a galvanometer-deflection caused by the effect is read and the compensation-method, in view of the fact, that the latter, although in general to be preferred, as it allows the elimination of various disturbances, is very troublesome, when small effects have to be measured. The differential-galvanometer used was of the KELVIN-pattern with a volt-sensibility of 5×10^{-8}; it was iron shielded and was mounted according to JULIUS. As to the resistance measurements these were partly performed in immediate connection with the determination of the HALL-effect, in which case the resistance of the plate used for this purpose was at the same time measured, partly (by means of the compensation-apparatus) with wires which were wound on thin sheets of mica and could be placed either at right angles to the field or parallel to it, the latter specially with a view to investigating the considerable difference between the transverse and the longitudinal effect, which difference develops specially at helium-temperatures.

§ 2. *Bismuth.* In accordance with frequent practice (e. g. by KAMERLINGH ONNES and BECKMAN) we used this substance in the form of pressed plates. The peculiarities in the resistance observed by STREINTZ with conductors of compressed powder, — although occurring also in our plates at higher temperatures — were not observable, when the plates were cooled below 0° C

The plates which served for our investigation were pressed in a steel mould and heated to about 200° C. in an electric furnace. When made in this way the granular structure was still clearly observable with a magnifying glass. The plate Bi_{VI} was made without special precautions; with plate Bi_{VII} the metallic powder was specially dried before moulding it. Bi_{VI} gave an abnormally high temperature-coefficient at higher temperatures and even after 36 hours' heating had not yet attained a constant resistance.

The metastable condition which according to Professor E. COHEN is peculiar of most metals as mixtures of different modifications manifested itself also in our experiments. The plates after being heated in the electric furnace to 60° or 100° C. showed some difference as regards resistance and HALL-effect after cooling, with the further peculiarity, that this change took place, although no change in the specific gravity, affecting the second decimal place could be established.

The results are contained in tables I and II.

TABLE I.

Bi_{VI}				
H	$-R$	Resistance	$-R$	Resistance
	$T=289°$ K		$T = 20°5$ K	
2400 Gauss	7.71	$2.5 \cdot 10^{-3}\,\Omega$		$3.7 \cdot 10^{-4}$
2420 ,,			42.13	
4800 ,,	6.68		38.95	
7200 ,,	6.02		35.44	
9650 ,,	5.37		33.62	
11800 ,,			29.76	$1.1 \cdot 10^{-3}$
12000 ,,	4.65	$3.1 \cdot 10^{-3}\,\Omega$		

TABLE II.

Bi VII.				
H	$-R$	Resistance	$-R$	Resistance
	T=289° K.		T=20°5 K	
2420 Gauss	10.57	$2.4 \cdot 10^{-3}$	80.03	$3 \cdot 10^{-4}$
4800 „	9.48		78.31	
7200 „	8.11		75.15	
9650 „	7.26		72.51	
12000 „	6.28	$3.2 \cdot 10^{-3}$	70.82	$1.6 \cdot 10^{-3}$

§ 3. Hall-*effect in graphite.* The great change in the properties of graphite through even small admixtures appears clearly from the fact, that with different kinds of graphite the temperature-coefficient of the resistance may even differ in sign.

The material we started from in our experiments was fine graphite-powder, such as is used in electro-plating; the powder was first treated with acids and alkali and carefully dried; the forming of the plate was again carried out in a steel mould. The electrodes which gave some difficulty at first were finally contrived in the following manner: the powder was provisionally moulded to a plate under comparatively low pressure, the stamp was then lifted off and six small pellets of solder were laid on the plate, after which a high pressure was applied. By trial we succeeded finally in obtaining suitable plates of $^1/_3$ m.m. thickness with six point-electrodes of about $^1/_2$ m.m. diameter, penetrating through the whole thickness of the plate.

The influence of insufficient drying of the powder was very marked; such plates, as did not come up to standard as regards drying, did not reach their final resistance until the current had gone through for 6 seconds.

The following table contains the results. It may be specially noted that the temperature coefficient is positive and that the Hall-effect falls strongly from 20° K. to 14° K.

TABLE III.

Graphite.			
H	290° K	20°.5 K	14°.5 K
	+ *R*:	+ *R*:	+ *R*:
4800 Gauss	0.68	3.4	1.42
6000 ,,	0.68		
7200 ,,		3.39	
8400 ,,	0.68		1.52
9600 ,,		2.81	
11800 ,,	0.74	2.22	1.52

§ 4. *The* HALL-*effect in cadmium.* Two circular rolled-out Cadmium plates of 1 cm. diameter were experimented on. The results are found in the following table.

TABLE IV.

Cadmium.			
H	290° K	20°.5 K.	14°.5 K.
	+ *R*:	+ *R*:	+ *R*:
3000 Gauss		13.1 · 10−4	
3600 ,,	4.6 · 10−4		
4800 ,,		20.2 · 10−4	22.3 · 10−4
6000 ,,	6.3 · 10−4		
7200 ,,		20.6 · 10−4	23.4 · 13−4
8400 ,,	5.9 · 10−4		
9600 ,,		19.6 · 10−4	22.3 · 10−4
11800 ,,		17.6 · 10−4	19.1 · 10−4
12000 ,,	5.5 · 10−4		

§ 5. *The* HALL-*effect at helium-temperatures.* The method was the same as in the previous measurements. To check the results measurements were made both with the compensation-apparatus and with the differential-galvanometer. Five different plates were experimented upon in the helium-bath. These were chosen so, that they could be regarded as representatives of metals for which the HALL-effect is of a different type. Each set of six wires from the six electrodes of one plate was completely separated from the other sets in the cryostat.

The following plates were investigated.

1. A tin and a lead plate: both metals are supra-conducting at extremely low temperatures. Lead remains supra-conducting up to a considerable threshold-value of current. It may be added, that both are diamagnetic: as DE HAAS has shown, the diamagnetic properties are of great importance for the HALL-effect.

At hydrogen-temperatures the HALL-effect is still so small, that it escapes observation. It was found, that at 4°.25 K. both with tin and lead the effect can be very well measured, when the field is so high, that ordinary resistance is generated in the metals. As long as the field is low enough for the metal to remain supra-conducting, the HALL-effect, like the ordinary resistance, disappears.

2. A silver plate, as representative of the group of metals for which at the ordinary temperature the HALL-coefficient is of the order of magnitude 10^{-4}; silver is diamagnetic and does not become supra-conducting at helium-temperatures.

As appears from the table, it was found that with silver also the HALL-effect increases, when the temperature falls to 4°.25 K. At still lower temperature it does not show any futher change, no more than the resistance without a field.

3. A bismuth-plate Bi_{VIII}, moulded from electrolytic bismuth-powder. Bismuth has a very high HALL-effect at hydrogen-temperatures and the change from 20° K. to 14° K. is still very small. It is the strongest diamagnetic metal.

The table shows, that below 14° K. there is not much further change in the HALL-effect. From 71 at 20° K. R rises only to 85 at 4°.25 K.

4. A nickel plate a representative of the ferro-magnetic metals.

With nickel at higher temperatures the HALL-effect shows a tendency to saturation owing to the magnetisation of the metal (Comm. No. 129, 130, 132). At hydrogen-temperatures it disappears, although the resistance of the plate is still considerable. Probably this is connected with the fact, that notwithstanding the already fairly considerable field the magnetisation of the nickel is still very small.

The results are collected in table V.

TABLE V.

Measurements in Helium.		
H	*R*	
	1. *Sn* (tin)	
	a. $T = 4^\circ.25$ K	
11300 Gauss		$+2\ 6 \cdot 10^{-5}$
	b. $T = 2^\circ.8$ K	$+9.8 \cdot 10^{-5}$
	2. *Pb* (lead)	
	a. $T = 4^\circ.25$ K	
300 ,,		$< 6 . 10^{-5}$
1000 ,,		$< 2 \cdot 10^{-5}$
5000 ,,		$+0.8 \cdot 10^{-5}$
11300 ,,		$+1.8 \cdot 10^{-5}$
	b. $T = 2^\circ.8$ K	
300 ,,		$< 6 \cdot 10^{-5}$
11300 ,,		$+1.3 \cdot 10^{-4}$
	3. *Ag* (silver)	
	a. $T = 4^\circ.25$ K	
11300 ,,		$16 \cdot 10^{-4}$
	b. $T = 2^\circ.8$ K	
11300 ,,		$16 \cdot 10^{-4}$
	4. *Ni* (nickel)	
	a. $T = 4^\circ.25$ K	
1300 ,,		$< 5 \cdot 10^{-5}$
11300 ,,		$< 1 \cdot 10^{-5}$
	b. $T = 2^\circ.8$ K	
13000 ,,		$< 1 \cdot 10^{-5}$
	5. *Bi*	
	$T = 4^\circ.25$ K	
1000 ,,		86 · 3
5000 ,,		84 · 2
11300 ,,		85 · 7

§ 6. *Change of the resistance in the magnetic field.* It was found that specially at helium-temperatures this change is very considerable, but that at 20° K. also it is still quite well measurable. In general there is a difference between the longitudinal and the transverse effects, which begins to show itself especially clearly at helium-temperatures.

We shall give our results in the form of curves (fig. 1 to 6) on which the numerical values may also be read with sufficient accuracy by using the scale indicated in the figures. So far the measurements both at hydrogen- and helium-temperatures have not gone beyond 12000 Gauss. They will afterwards be further extended to higher field-strengths especially at hydrogen-temperatures.

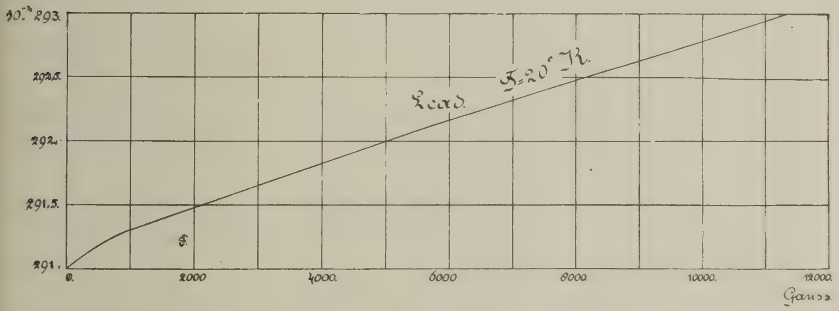

Fig. 1.

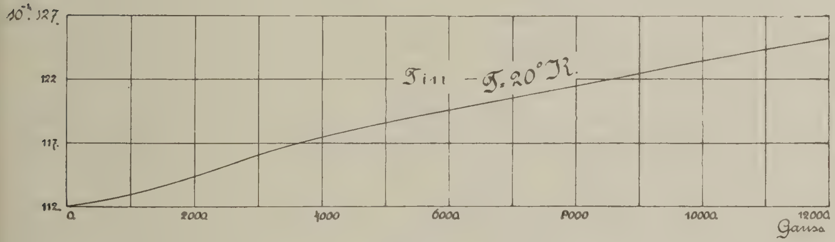

Fig 2.

Figs. 1 and 2 contain the results for the resistance of lead and tin in a magnetic field. The difference between the longitudinal and transverse effects was not more than the errors of the measurements. The abscissa gives the ratio of the resistance to that at 0° C.

Fig. 3 and 4 represent the longitudinal and transverse effects

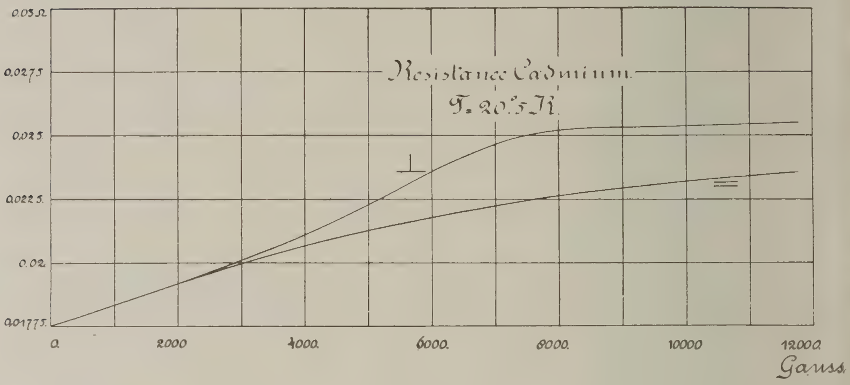

Fig. 3.

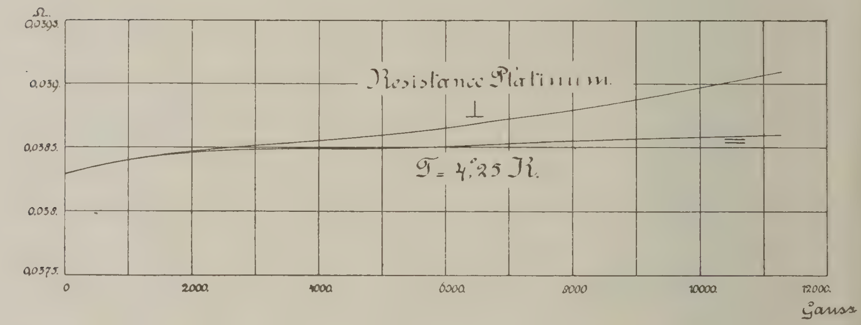

Fig. 4.

for cadmium and for platinum. The abscissae give directly the resistance in Ohms.

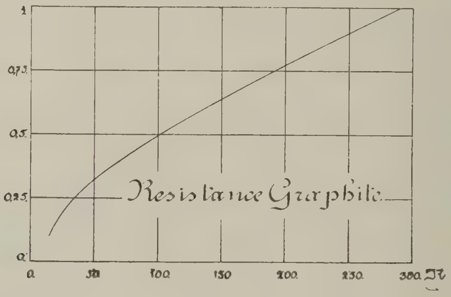

Fig. 5.

Fig 5 en 6 show the results for graphite, Fig. 5 the dependence of the resistance on the temperature, fig. 6 the dependence on the magnetic field.

We have further made measurements on the resistance of a

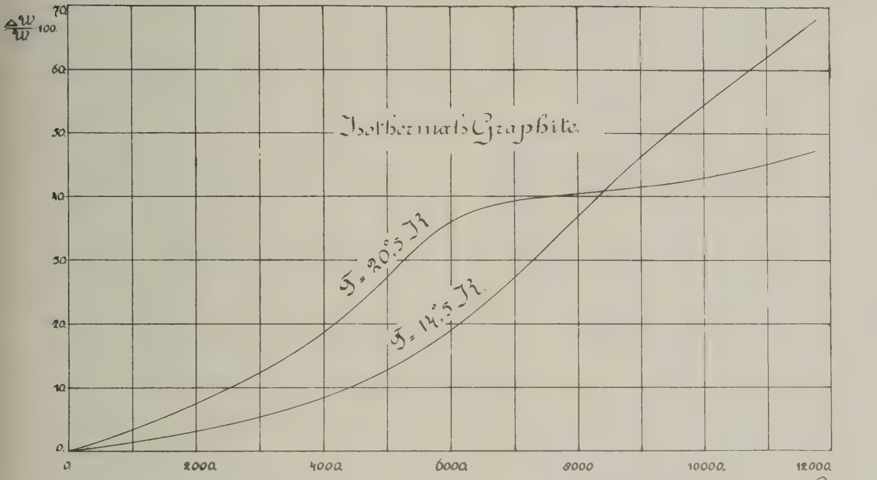

Fig. 6.

plate of not-purified graphite. These are not concluded, howewer, and will be published later together with measurements on polarisation-phenomena which may possibly show themselves with pressed graphite.

COMMUNICATIONS

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N°. 142^c.

◆

H. KAMERLINGH ONNES and G HOLST. Further experiments with liquid helium. M. Preliminary determination of the specific heat and of the thermal conductivity of mercury at temperatures, obtainable with liquid helium, besides some measurements of thermoelectric forces and resistances for the purpose of these investigations.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*,**26 September 1914**, p. 703—710).

EDUARD IJDO. — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and G. HOLST. *Further experiments with liquid helium. M. Preliminary determination of the specific heat and of the thermal conductivity at temperatures, obtainable with liquid helium, besides some measurements of thermoelectric forces and resistances for the purpose of these investigations.*

(Communicated in the meeting of June 27 1914).

§ 1. *Introduction.* Measurements of the specific heat and of the thermal conductivity of mercury were considered to be of special importance with a view to the discontinuity, found at 4°.19 K. in the galvanic resistance of this metal. The preliminary results have been already mentioned in Comm. N°. 133, for the measurements were carried out as early as June 1912. We wished to repeat the experiments, which we considered only as a first reconnoitring in this region, because our opinion was that, by some inprovements in the experiments, the accuracy of the results could be considerably increased. Special circumstances frustrated this, and now as there seems to be no prospect of a repetition, in the mean time we communicate the details of our investigation.

§ 2. *Thermoelectric forces.* The first difficulty in these determinations was the choice of a suitable thermometer. The measurements already performed about the resistance of platinum, gold and mercury did not give much hope, that there would be among the metals a suitable material for resistance thermometers. We have therefore investigated a series of thermoelements. The gold-silver couple, a suitable thermometer at hydrogen-temperatures [1]), showed down to the higher helium temperatures a fairly large thermoelectric power, at the lower helium temperatures, however, the thermoelectric power diminishes rapidly, so that this couple did not satisfy the requirements. Moreover, this couple was not at all free from disturbing electromotive forces, which appeared at places of great fall of temperature in the cryostat. Nearly all other elements were subject to the same fault. But apart from this, none of the combinations was suitable. Notwithstanding we communicate the results of our determinations, because they show clearly, that according to the theoretical investigations of Nernst and Keesom [1]), the thermoelectric power of all couples investigated approaches to zero at heliumtemperatures. The different wires were measured against copper. After a preliminary research, which included also the determination of the thermoelectric forces of nickel and of six gold-silver alloys, the following combinations were selected as most promising for investigations in liquid helium.

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[1]) Compare H. Kamerlingh Onnes and J. Clay, Comm. No. 107*b*.

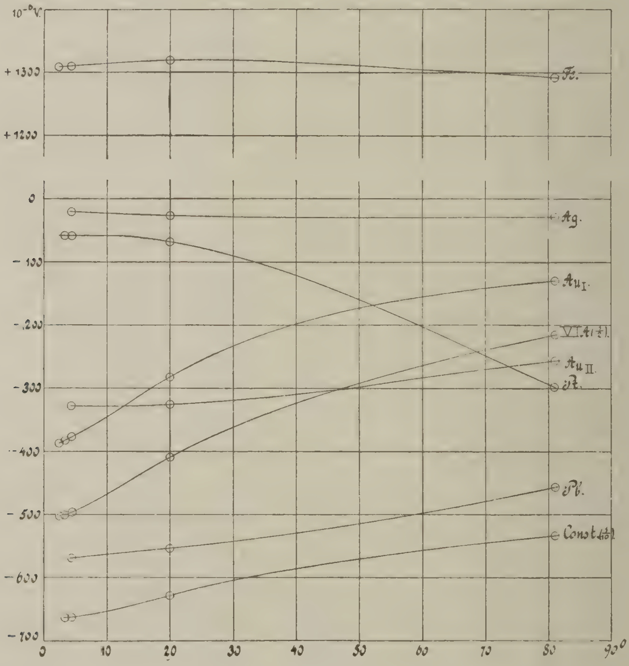

Fig. 1.

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[1]) W. Nernst, Theor. Chem. 7e Aufl. 1913 p. 753. Berl. Sitz. Ber. 11 Dez. 1913 p. 972.

W. H. Keesom, Leiden Comm. Suppl. No. 30*b* (May 1913).

Thermoelectric forces against copper.

T	*Ag*	Au_1	Au_2	*Pt*	*Pb*	*Fe*	Constantin	VI A1)
81°K.	—28	—129	—257	—298	—457	+1293	—5320	—432
20°	—28	—282	—326	—68	—553	+1319	—6280	—819
4°26	—21	—375	—328	—58	—559	+1309	—6630	—990
3°20	—	—383	—	—59	—	+1309	—6630	—1002
2°26	—	—386	—	—	—	—	—	—1004

Figure 1 shows their thermoelectric forces against copper, at the absolute temperature *T*, given in the first column of the table. The temperature of the second juncture was 16° C.

§ 3. *Change of the resistance of alloys with temperature.* As it appeared impossible to find a suitable thermo-couple, our attention was drawn to the change of resistance of constantin, which had already been measured at hydrogen temperatures by KAMERLINGH ONNES and CLAY. This alloy shows here a considerable decrease of resistance at decreasing temperature; it was, therefore, probable that constantin could be suitably used as a resistance thermometer at helium-temperatures. Experiments have shown, that this was in fact the case. Later measurements (see Comm. N⁰. 142*a* § 4) proved that also manganin, whose resistance begins to diminish at decreasing temperature and which has at oxygen temperatures a considerable smaller resistance than at ordinary temperatures, is fit for temperature measurements in liquid helium.

§ 4. *Specific heat of mercury. a. Experimental arrangements.* The method, used in the determination of the specific heat agrees most with the one used by NERNST in his investigations about

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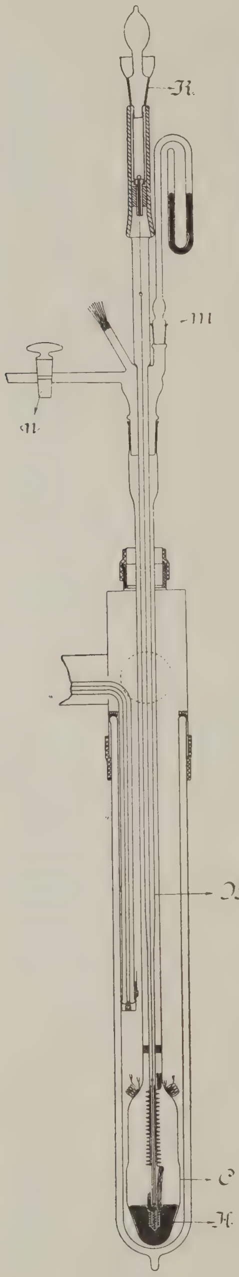
1) *Au* with 0.476 weight % *Ag*.



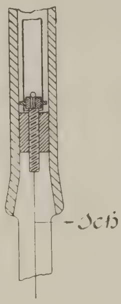


Fig. 2.

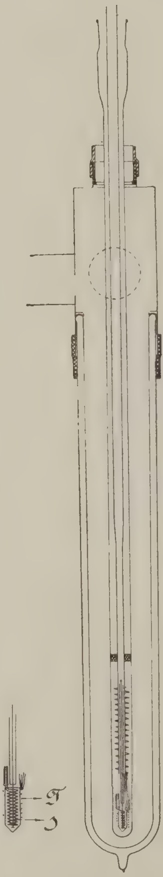


Fig. 3.

the specific heat. A little block of solid mercury hung freely in a high vacuum and was heated electrically. The increase of temperature was determined by means of a constantin resistance thermometer. To obtain the little block of mercury the liquid metal (comp. fig. 2 with magnified fig. of details) was poured into the vessel *C* through a capillary, provided with a funnel, which could be introduced through *m*. First *C* was in the same way supplied by means of a funnel with a small quantity of pure pentane, which, at the introduction of the mercury, remains as a thin layer between the glass and the mercury. A little hollow steel cylinder (thickness of the wall $^1/_{20}$ m.m·), which contained the heating wire — a constantin wire, insulated with silk and covered with a thin layer of celluloid to avoid all electrical contact with the mercury --- was immersed in the mercury. Round this cylinder a second constantin wire was wrapped, which was to be used as a thermometer. The little cylinder was, by means of silk wires (stiffened by celluloid) fixed to a little glass rod, which could be moved up and down through the tube *B*, and which was centred by constrictions in this tube. This glass rod was connected to a silk wire, which could be screwed up and down by turning the handle *K*. Now the mercury was frozen by cooling down to the temperature of liquid air. The thin layer of pentane, which is spread over the glass, acts as a viscous lubricant at this temperature and prevents the sticking of the mercury to the wall in freezing. After having been frozen, the little block of solid mercury was screwed up by means of the handle *K* and the temperature was increased to about − 50° C. Thereupon a high vacuum was established by means of a GAEDE mercury pump and the pentane was distilled off into a tube, immersed in liquid air. During the experiments the heat insulation of the block appeared to be so good, that the temperature remained many degrees above that of liquid helium, although it was let down against the glass wall. Therefore a little gas had to be admitted in order to cool the block. This manipulation succeeded perfectly, but the gas could not be removed quickly enough in the short time available for the experiments. The loss of heat of the mercury was thus very considerable (decrease of the temperature difference to half of the original value in about 100 seconds) and therefore the correction, to be applied to the increase of temperature while heating, remains the greatest source of uncertainty. Nevertheless it seems possible, that the results are accurate to about 10 %.

The thermal capacity of the hollow steel cylinder with the thermometer and the heating was determined afterwards by a separate experiment. Fig. 3 shows the apparatus used for this purpose.

b. Results. Measurement at the boiling point of helium. The quantity of heat supplied to the mercury amounted to 1,10 cal, the increase of temperature, corrected for the loss of heat during the period of heating, was 2,22 degrees K. whilst the quantity of heat, necessary to heat the little steel cylinder with the thermometer 2,22 degrees, amounted to 0.11 cal. (result of a separate experiment). Control experiments showed that the heating wire (used as a thermometer) and the thermometer wire outside the steel cylinder had the same temperature. The mass of the mercury was 314 grammes, so that 0.00142 cal./degree K. was obtained for the mean specific heat between 4°.26 K. and 6°.48 K.

The relation of GRÜNEISEN [1] $\frac{w}{T} \sim c_p$ would have given $c_p = 0.0037$ for 4°.27 K.

Measurement at 3°.5 K. Afterwards the experiment was repeated at the temperature of liquid helium, boiling under a pressure of 6 cm. of mercury; 0.000534 cal./degree K. was found for the mean specific heat between 2°.93 K. and 3°.97 K.

Assuming this mean value of the specific heat, we shall calculate now the value of this magnitude for a definite temperature according to DEBIJE's formula, which holds for our very low temperatures

$$c = C \, . \, T^3,$$

so that the mean specific heat between two temperatures T_1 and T_2 is

$$\bar{c} = \frac{C\,(T_1^4 - T_2^4)}{4\,(T_1 - T_2)}.$$

We obtain from both experiments $C = 0.0000088$ and 0.0000127 respectively. The agreement is not satisfactory; although, taking into account that the absolute temperature occurs in the formula in the 4th power, and that therefore small deviations in T involve very large ones in C, we may safely conclude from experiments, that, *with respect to the specific heat, nothing peculiar happens at the point of discontinuity*, and that we may content ourselves with a preliminary mean value $C = 0.0000110$ when we assume for the moment, that the specific heat does not show any discontinuity at all.

We have then

$$c = CT^3 = 0.0000110 \, T^3.$$

or for a gramme-molecule

$$c = 0.00220 \, T^3.$$

For the characteristic constant Θ, introduced by DEBIJE we find with $c_\infty = 5.96$ and

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[1] E. GRÜNEISEN, Verh. d. D. Phys. Ges. 1913 p. 186.

[2] Compare KAMERLINGH ONNES and HOLST, Leiden Comm. No. 142*a*, June 1914.

$$c = 0.00220\,T^3 = 77.938\frac{T^3}{\Theta^3}c_\infty = 464\,\frac{T^3}{\Theta^3}$$

$$\Theta = 60.$$

As a matter of fact, the specific heat has been determined here at constant pressure and not at constant volume. In the foregoing calculation, the difference of the specific heats c_v and c_p, given by

$$c_v = c_p - A c_p^2\,T,$$

has been neglected. Indeed, A is about $7.2 \cdot 10^{-5}$ and c_p and T are both small.

Using DEBIJE's formula, we can compare our results with those of POLLITZER [1]) at somewhat higher temperatures. For this purpose we calculate a value of Θ agreeing as well as possible with POLLITZER's figures of $\frac{c}{c_\infty}$, we find then 110. In fig. 4 c_v is plot-

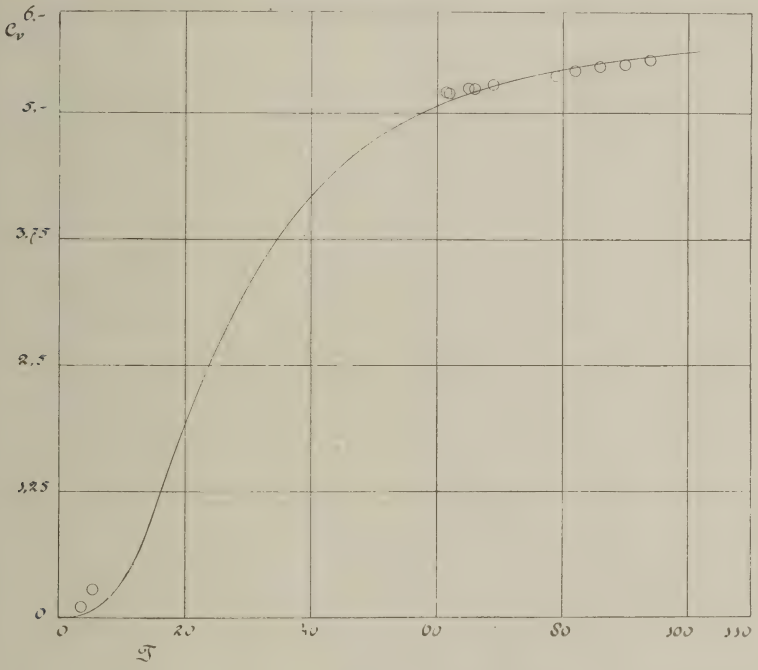

Fig. 4.

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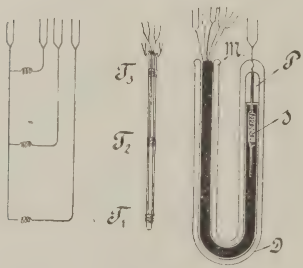
1) See F. POLLITZER. Zeitschr. f. Elektrochem. 1911. p. 5.

ted as a function of T according to DEBIJE; the values, determined experimentally, are indicated by circles.

The accordance at helium temperatures is bad as could be expected in consequence of the difference between the value of Θ used in the calculation, and the one deduced from our experiments. Meanwhile we remark, that in POLLITZER's experiments too a distinct deviation from DEBIJE's curve is to be noticed, in the sense of a decrease of Θ (about $115-102$) with decreasing temperature, which would be, according to our experiments, very considerable down to helium temperatures; further that, according to LINDEMANN's formula and by comparison with lead (88), $\Theta = 61$ is to be expected for mercury.

§ 5. *The thermal conductivity.*

The thermal conductivity was determined by means of the apparatus, represented in figure 5. A *U*-shaped tube, with double walls, and closed at one end, was provided with mercury. The closed branch contained a constantin wire S, insulated by means of celluloid, which made contact with the mercury at the free end. This wire was used as a heating wire. The current returned through the mercury itself by means of a wire, in contact with the mercury at the open end of the tube. The fall of temperature was measured with 3 constantin thermometers T_1, T_2 and T_3 consisting of wire of $^1/_{50}$ mm. thickness, wrapped around a small glass tube. The experimental arrangement is further explained by the diagrammatic figure. All wires were connected to each other by two wires, insulated by thin layers of celluloid and further running free through the liquid helium.



Fig, 5.

In consequence of a wrong manipulation during the preparation, the tube had lost a little mercury, so that only the two lower thermometer wires could be used. The heat developed in the heating wire and the difference in temperature thus produced were measured at two different temperatures, the one above and the other one below the point of discontinuity in the electrical resistance. The section of the cylinder of solid mercury amounted to 0.47 cm^2, the distance of the thermometers to 5.0 cm.

At the boiling point of helium the supplied energy was 0.633 watt/sec., the difference in temperature produced 0.58; at 3°.7 K. 0.0365 watt/sec. and 0.23.

From this we find for the mean thermal conductivity between 4°.5 K. and 5°.1 K. $k = 0.27$ cal/cm. sec. and between 3°.7 K. and 3°.9 K: $k = 0.40$ cal/cm. sec.

The thing, which immediately strikes us, is that there is here no distinct discontinuity as was found at 4°.19 K in the electrical conductivity, although the thermal conductivity becomes much larger, when the temperature decreases. As there do not exist direct determinations for solid mercury, we only can make a rough estimation with the aid of WIEDEMANN and FRANZ's law.

At the melting point, the electrical conductivity of liquid mercury amounts to $1.10\ 10^4$ cm.$^{-1}$ Ω^{-1} and of solid mercury to about five times as much, thus to $5.50\ 10^4$ cm.$^{-1}$ Ω^{-1}. From this we find by comparison e.g. with lead about 0.075 for the thermal conductivity. The values here obtained in liquid helium are 3.5 and 5.5 times as large.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 142^d.

* * *

H. KAMERLINGH ONNES and H. A. KUYPERS. Measurements on the capillarity of liquid hydrogen.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **27 Juni 1914**, p. 501—505).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES and H. A. KUYPERS. *Measurements on the capillarity of liquid hydrogen.*

For the determination of the capillary constant of liquid hydrogen in contact with its saturated vapour the method of capillary rise was used. The apparatus are in the main arranged in the manner as used for other liquid gases in Comm. N⁰. 18. The part of the apparatus which serves to condense the gas in the wide experimental tube (fig. 1), inside which is the capillary, is similar to the corresponding part which may be seen on plate I A of Comm. N⁰. 107*a*; the tube of fig. 1 is sealed in at g_2.

The radii of the sections of the tubes were found by calibration with mercury as follows:

radius of the capillary inside $r = 0.3316$ cm
„ „ „ „ outside $r_1 = 0.0801$ cm
„ „ „ surrounding tube inside $R = 0\ 554$ cm

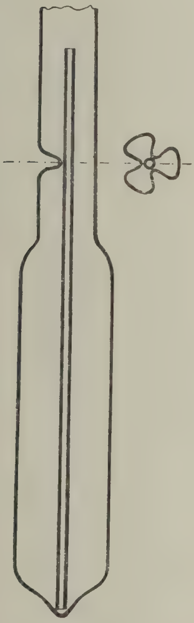


Fig. 1.

Measurements of the capillary rise. The reading of the ascension gave some trouble as it had to be made through a number of glass vessels and baths. The rise was measured with a cathetometer; to test the accuracy of the readings they were taken one time on a millimetre-scale which had been etched on the capillary and another time directly on the scale of the cathetometer. When it was found, that there was no difference between the heights obtained in the two ways, they were afterwards only measured by means of the scale of the cathetometer, because, when the cryostat was filled with the different liquid gases, the divisions on the capillary were difficult to distinguish owing to the rising gas-bubbles in the liquids.

Temperature. The temperature was deduced from the pressure of the vapour in the hydrogen-bath using the vapour-pressure curve (H. KAMERLINGH ONNES and W. H. KEESOM, Comm. N^0. 137*d*, table on page 41).

Observations. The heights measured and the corresponding temperatures of the hydrogen are contained in the following table. Repeated measurements show, that the accuracy of the reading of the rise may be estimated at 0.002.

TABLE I.

Temperature in KELVIN-degrees.	Rise in cms.
20.40	1.616
18.70	1.794
17.99	1.869
16.16	2.064
14.78	2.209

The observed heights (h) have to be corrected for the curvature of the surfaces by means of the following formulae: (1) the correction for the meniscus in the narrow tube is $\frac{r}{3}$[1]). (2) the correction for the ring-shaped meniscus is (according to VERSCHAFFELT Comm. N^0. 18).

$$h' = \left(h + \frac{r}{3}\right) \frac{\dfrac{2d}{(R - r_1{}^2)}}{\dfrac{1}{r} - \dfrac{2d}{(R - r_1)^2}}$$

For this correction the height of the ring-shaped meniscus, as the minor axis of the elliptical section with a meridian plane, is required to be known. With the illumination used this height could not be measured accurately. Afterwards for further correction we hope to be able to determine its value by special measurements: in the mean time the section was assumed to be circular which will give a close approximation. The corrected values are given in column 6 of table II.

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[1]) LAPLACE, Méc. Cél. Tome X, Supp. § 5, Paris 1805.
id. , Oeuvres Tome IV, p. 415, Paris 1845.
ALLAN FERGUSON, Phil. Mag., (6) 28. 1914, p. 128.

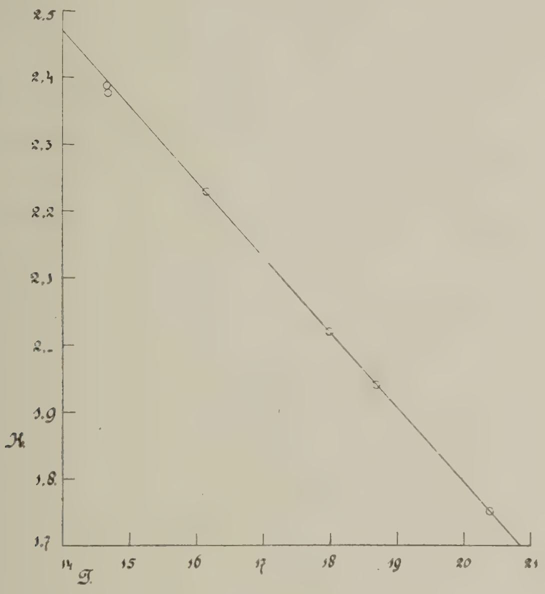

Fig. 2.

When the capillary rise is plotted as a function of the temperature — fig. 2 —, a straight line is obtained. The constants determined from this line give the formula

$$H = -0.1124\ T + 4.044.$$

This formula gives $H = 0$ for $T_{H=0\,\text{extrap.}} = 35.98^\circ$ K.

Assuming the critical temperature as $T_k = 31.11^\circ$ K (mean of DEWAR, OLSZEWSKI and BULLE[1])) it is seen, that the formula, as was to be expected, does not hold up to the critical temperature and that the curve which gives the dependence of H on the temperature has its concave side towards the temperature-axis. The difference $T_{H=0\,\mathrm{extrap.}} - T_k$ for hydrogen amounts to

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[1]) F. BULLE, Physik. Zeitschr. XIV, 1913, p. 860.

$$T_{H=0\,\mathrm{extrap.}} - T_k = 3.87.$$

If $T_{H=0\,\mathrm{extrap.}} - T_k$ is divided by the critical temperature the positive value $\frac{3.87}{32.1} = 0.125$ is obtained. For methyl-chloride [1]) and ethylether [2]) similar values are obtained [3]).

Surface-tension. From the capillary rise the surface-tension ψ_σ is found by means of the following formula:

$$H = \frac{2\psi_\sigma}{(\rho_{\mathrm{liq.}} - \rho_{\mathrm{vap.}})g}\left(\frac{1}{r} - \frac{1}{R - r_1}\right).$$

TABLE II.

Temp.	h	Correction for the meniscus		H	ρ_{liq}	$\rho_{\mathrm{vap.}}$	$\rho_{\mathrm{liq.}} - \rho_{\mathrm{vap.}}$	ψ_σ observ. dyn. cm.	O—C
		inside	outside						
20.40° K	1.616	0.011	0.122	1.749	0.0708	0.0013	0.0695	$2\ 12^6$	$-0\ 01^1$
20.39^5	1.617	11	122	1.750	708	13	695	2.12^7	-0.01^1
20.39	1.619^5	11	122	1.752^5	708	13	695	2.13^0	-0.09^9
18.70	1.794	11	136	1.941	726	08	718	2.43^8	-0.00^5
17.99	1.869	11	141	2.021	733^5	05	728^5	2.57^5	$+0.00^4$
16.16	2.064	11	156	2.231	751	03	748	2.91^9	$+0.01^9$
14.68^5	2.199	11	166	2.376	764	02	762	3.16^7	$+0\ 00^4$
14.66	2.209	11	167	2.387	764	02	762	3.18^2	$+0.01^5$

The densities for liquid hydrogen are taken from the observations by H. KAMERLINGH ONNES and C. A. CROMMELIN (Comm.

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[1]) According to measurements by J. E. VERSCHAFFELT; comp. A. VAN ELDIK, Comm. N°. 39, p. 14.

[2]) E. C. DE VRIES, Comm. N°. 6.

[3]) The corresponding figures (deduced, however, from not-corresponding temperature ranges) are 0.038 and 0.017 respectively.

N^0. 137*a*). For the calculation of the vapour-densities use is made of the second virial-coefficient, as deduced from the measurements by H. KAMERLINGH ONNES and W. J. DE HAAS (Comm. N^0. 127*c*).

With these data the values of ψ_σ in table II are calculated. Under O—C are given the differences between $\psi_{\sigma\,\text{obs.}}$ and values of ψ_σ calculated from VAN DER WAALS's formula

$$\psi_\sigma = A\,(1 - \mathfrak{t})^B$$

where

$$A = 5.792$$
$$B = 0.9885$$

From the value found for B it appears, that ψ_σ as a function of T is nearly a straight line.

The constant in EÖTVÖS's formula for hydrogen deviates considerably from the value 2.12, found by RAMSAY and SHIELDS [1]) as the average for a number of normal substances. In Table III the values of $k_{\text{Eö}}$ for a few of these substances, together with those for some liquid gases, are collected. As observed by KAMERLINGH ONNES and KEESOM (note 381 Suppl N^0. 23), normal substances form a series in this respect, on the whole progressing with the critical temperature (although with deviations which may be ascribed to particularities in the law of molecular attraction, e. g. with oxygen)

TABLE III.

Ethylether [2])	2.1716
Benzene [2])	2.1043
Argon [3])	2.020
Nitrogen [3])	2.002
Carb. monoxide [3])	1.996
Oxygen [3])	1.917
Hydrogen	1.464

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[1]) RAMSAY and SHIELDS. J. chem. soc. 63 (1893); ZS. f. physik. Chem. 12 (1893).

[2]) RAMSAY and SHIELDS ZS f. physik. Chem. 12 (1893), 15 (1894).

[3]) BALY and DONNAN, J. chem soc. 81 (1902).

A calculation of the constant k' in EINSTEIN's formula [1])

$$\left[\left(\psi_\sigma - T\frac{d\psi_\sigma}{dT}\right) v^{\frac{2}{3}}_{\text{liq. } M} = k'\left(\lambda_{M,p=1} - RT\right)\right]_{T=20.33}$$

for hydrogen gives

$$7.34 \times 10^{-9}.$$

The fact, that hydrogen appears to have a considerably higher value of k' than that calculated by EINSTEIN for benzene (5.3), might, in view of the theory underlying the formula, indicate, that for hydrogen the sphere of molecular action reaches in the liquid to further layers of surrounding molecules than for substances like benzene.

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[1]) A. EINSTEIN, Ann. d. Phys. 4. 34, 1911, p. 165.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

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Director of the Laboratory.

N°. 143.

W. H. KEESOM and H. KAMERLINGH ONNES. The specific heat at low temperatures. I. Measurements on the specific heat of lead between 14° and 80° K. and of copper between 15° and 22° K.

(*Translated from: Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam*, **31 October 1914**, p. 792—812).

EDUARD IJDO — PRINTER — LEIDEN.

W. H. KEESOM and **H. KAMERLINGH ONNES**. *The specific heat at low temperatures.* I. *Measurements on the specific heat of lead between* 14° *and* 80° K. *and of copper between* 15° *and* 22° K.

§ 1. *Introduction.* Soon after the methods of obtaining baths of temperatures which are accurately known and can be kept constant for a long time, in the range between the boiling point and the melting point of hydrogen, had been worked out [1]) in the cryogenic laboratory at Leiden, a series of investigations on the calorimetry at very low temperatures was started there. DEWAR's measurements on the mean specific heat of different substances between the temperature of liquid air and the boiling-point of hydrogen [2]) had particularly drawn attention to the interest of those investigations. The continuation of his experiments in the still lower region of temperatures mentioned above seemed very desirable [3]). As was done by DEWAR the series of investigations in this direction was begun by determinations of the heat of vaporisation of hydrogen. A report on the first results of those determinations was given at the Dutch Congress of Science and Medicine at Groningen (1911) [4]). An investigation regarding the specific heat af lead, after which other metals were to follow, at hydrogen temperatures, an investigation which had a particular interest with a view to EINSTEIN's theory and also in connection with [5]) NERNST's theorem, was announced on that occasion.

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[1]) Cf. specially H. KAMERLINGH ONNES, Comm. N^0. 94*f* (Sept. '06) and H. KAMERLINGH ONNES, C. BRAAK and J. CLAY, Comm. N^0. 101*a* (Dec. '07).

[2]) J. DEWAR, Proc. Roy. Inst. March 25, 1904, Proc. Roy. Soc. A 76 (1905) p 325, later more extensively between the boiling point of nitrogen and that of hydrogen: Proc. Roy. Soc. A 89 (1913) p. 158.

[3]) This was pointed out at the Ist International Congress of Refrigeration at Paris 1908. H. KAMERLINGH ONNES, La liquéfaction etc. Note I. Sur les expériences à faire aux températures très basses. Leiden Comm. Suppl. N^0. 21*a* p. 29.

[4]) W. H. KEESOM. The heat of vaporisation of hydrogen. Handel. 13de Ned. Nat. en Geneesk. Congres, April 1911, p. 181. Published also Leiden Comm. N^0 137*e*.

[5]) Cf. also H. KAMERLINGH ONNES. Reports of the IInd International Congress of Refrigeration. Vienna 1910 (Leiden Comm. Suppl. N^0. 21*b* p. 42).

Since then in Nernst's laboratory a highly important series of investigations on the specific heat has been made by himself and by his collaborators [1]). In particular the investigations on solids at low temperatures, which had already been made down to the temperatures of liquid air boiling under reduced pressure, were continued to the temperatures which can be obtained with liquid hydrogen. Besides Kamerlingh Onnes and Holst [2]) made preliminary measurements of the specific heat of mercury at helium temperatures. The investigations mentioned have already furnished a great number of highly valuable data, which in particular have served for a test of the theories of Debije [3]) and of Born and v. Kármán [4]). Notwithstanding all that, and although, moreover, the method we followed is mainly that which has been developed by Nernst and Eucken, the continuation of our programme seemed yet to remain desirable. First, when Nernst's investigations had followed the specific heat down to the region of hydrogen temperatures, because only a few of his observations entered into this region and the accuracy of the observations left some doubt with Nernst himself, and later when between the boiling point and the melting point of hydrogen also more accurate determinations had been made in his laboratory [5]), because for the investigation of the questions which have now come to the front a high degree of accuracy is desirable.

In this respect it was an advantage: 1st that particularly by the investigation of Kamerlingh Onnes and Holst [1]) on the scales of the hydrogen and the helium constant volume thermometers we could avail ourselves of a more accurate temperature scale [2]); 2nd that the cryostats used at Leiden allowed the measurements to be performed under more favourable circumstances in other respects also. In fact in the measurements published in this paper an accuracy of 2% has been reached at hydrogen temperatures, while there is reason to expect that in subsequent measurements the accuracy will still be considerably increased.

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[1]) For the literature we refer to Leiden Comm. Suppl. N° 23 "Die Zustandsgleichung" Math. Encycl. V. 10 Note 838. Later: A. Eucken and F. Schwers. Verh. d. D. phys. Ges. 15 (1913) p. 578. W. Nernst and F. Schwers. Berlin Akad. Sitz. Ber. 1914 p. 355. R. Ewald. Ann. d. Phys. (4) 44 (1914) p. 1213.

[2]) H. Kamerlingh Onnes and G. Holst. Comm. N°. 142*c* (Sept. '14).

[3]) P. Debije. Ann. d. Phys. (4) 39 (1912), p. 789. W. Nernst and F. A. Lindemann. Berlin Akad. Sitz. Ber. 1912, p. 1160. Cf. also W. Nernst, Vorträge Wolfskehl Congress Göttingen 1913, p. 61.

[4]) M. Born and Th. v. Kármán. Physik. ZS. 13 (1912), p. 297; 14 (1913), p. 15, 65. H. Thirring, Physik. ZS. 14 (1913), p. 867; 15 (1914), p. 127, 180. Cf. M. Born, Ann. d. Phys. (4) 44 (1914), p. 605.

[5]) A part of our observations had already been made when the results of Eucken and Schwers were published (see § 5). The completion of even the limited part of the programme, which is contained in this communication, has been much retarded, partly by the wish to attain very trustworthy results.

§ 2. *Method. Apparatus.* We followed with some modifications the method which has been in particular developed by Nernst and Eucken, and which has shown itself to be very suitable for low temperatures. In this method a block of the metal to be investigated, provided with wires for heating and temperature measurement, is suspended in a vacuum which is made as perfect as possible. Within the block a measured quantity of heat is developed by an electric current, and the increase of temperature produced is measured.

Fig. 1 represents the cryostat with the calorimeter. To protect the block against the residual heat radiation which enters the calorimeter vessel C (the vacuum-vessels are silvered a slit being left open), it is silvered on the outside up to a few mms. below the sealing places C_2 of the platinum wires. Moreover the plate C_1, which through a platinum wire is in heat conducting connection with the bath, prevents radiation from above.

In the block B of the metal to be investigated a chamber has been drilled, into which the core K fits tightly. This core contains the wires which serve for heating and for measuring the temperature; when the temperature wire has once been calibrated and the heat capacity of the core measured separately, it can serve for the successive measurements of the specific heat of all the metals of which suitable blocks can be made, and of other substances also when use is made of a suitable vessel. The core consists (Fig. 2) of a solid cylinder K_1, and two cylindrical mantles K_2 and K_3, all of copper, provided above with flat, tightly fitting collars, and of a copper plate K_4, which is in addition connected with K_1 by means of a copper screw. Round K_1 a gold wire has

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[1]) H. Kamerlingh Onnes and G. Holst. Comm. No. 141a (May 1914).

[2]) The temperature scale used by Nernst, and also those of Eucken and Schwers and of Nernst and Schwers are mainly based upon the older calibration of the thermometer Pt_I by Kamerlingh Onnes, Braak and Clay, which has to be replaced by the newer one of Kamerlingh Onnes and Holst. Cf. further § 3.

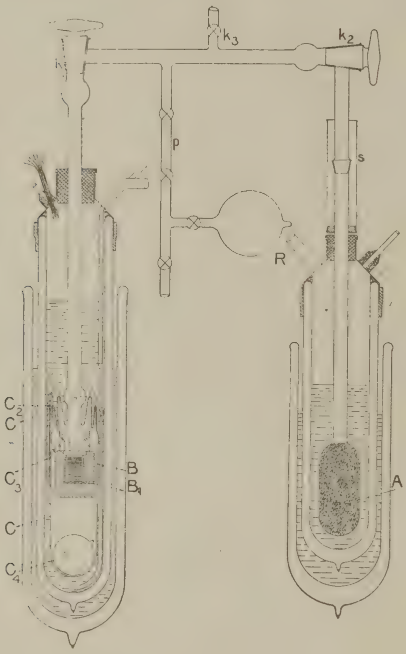

Fig. 1.

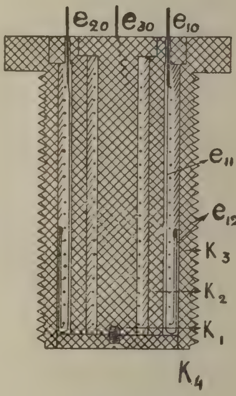

Fig. 2.

been wound doubled on itself; for insulation and at the same time for heat conduction enamel and thin paper were used; the electrodes $e_{10}, \ldots e_{40}$, stout platinum wires (1.5 mm.), which are led through the collars and insulated from these, and protrude outside the core, are rolled out below to flat bands which are a few centimeters longer than the cylinder; to the ends of these the gold wire is soldered with gold, after which the band was bent up ($e_{12} \ldots$) and fastened to the core and insulated.

The space which remained within K_2 was filled up with the copper-tin-amalgam which is used in dentistry. In the same way a constantin wire was wound round K_2 and enclosed between K_2 and K_3. Then the whole was closed by the plate K_4 below, and the different parts were united as much as possible by Wood-metal. The insulation was tested with an insulation meter and found to be more than sufficient.

The block B is suspended from two platinum wires (0.6 mm.) with the aid of two small glass rings. These platinum wires serve at the same time for conduction of the heating current. They are therefore connected to the electrodes of the constantin wires by platinum wires (0.2 mm.). For simplicity the wires, which serve for measuring the potential difference between the electrodes e_{10}, e_{20} of the constantin wire, are applied outside the calorimeter vessel near the sealing places. The resistance between these junctions and the ends of the constantin wire is inappreciable compared with the resistance of the latter (140 Ω). For the gold wire, which serves as a thermometer, potential as well as current wires (within the calorimeter vessel 0.1 mm. platinum, insulated with silk) lead directly to the electrodes.

The stopcocks k_1 and k_2 have wide borings, k_3 leads to a GAEDE mercury pump, which serves for evacuating the charcoal and for a preliminary evacuation of the calorimeter vessel, and to a Mc.-Leod gauge, R is a reservoir which is filled with hydrogen; with the aid of the pipette p a quantity of this hydrogen is admitted into the calorimeter when it is required to bring about heat conduction between the block and the bath.

The charcoal tube A, made of glazed opaque quartz, was filled with cocoa-nut charcoal, and evacuated for a sufficient time at 600° C. before each series of measurements. During the measurements it is cooled with liquid hydrogen

To diminish the exchange of heat between the metal block and the bath through the conducting wires, during the measurements the bath that surrounds the calorimeter was brought as nearly as possible to the temperature at which the measurement was to be made. The time-rate of the temperature before the heating and after the heating, at least after a few tens of seconds, was as a rule very small, if not inappreciable. For illustration in Fig. 3 and 4 the time-curve of the galvanometer, which indicates the temperature, during two measurements is represented, viz.

for a measurement of the specific heat of lead (Fig. 3) and for a measurement of the specific heat of copper (Fig. 4), respectively. The increase of temperature was in both cases about 1 degree

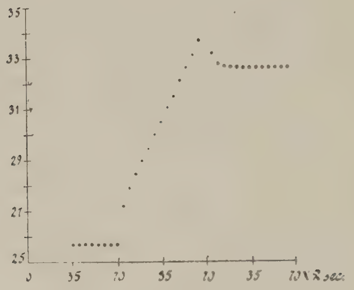

Fig. 3.

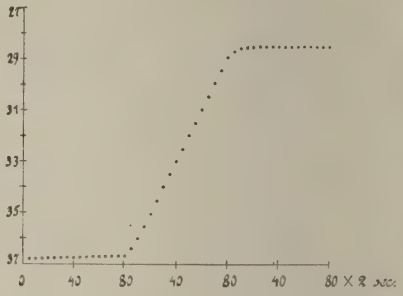

Fig. 4.

In the measurement with lead the temperature of the core appears to have risen about $^1/_6$ degree above the mean temperature of the lead block during the heating, in the measurement with copper, for which the heat supply per second was chosen smaller in accordance with the smaller specific heat, the corresponding temperature difference is not appreciable. Where necessary, corrections for the heat exchange with the bath were applied.

The heat supply. The arrangement for sending a current of measured intensity and potential difference during a definite time through the constantin heating wire is represented in Fig. 5 together with the arrangement [1]) for measuring the resistance of the gold thermometer wire. Intensity and potential difference were read on accurate Weston millivolt- and voltmeters. These were calibrated repeatedly for the measuring ranges used with the aid of a standard element of the Weston Cy., standard resistances and a compensation apparatus free from thermoelectric forces with an auxiliary apparatus according to Diesselhorst, all calibrated at the Physikalisch Technische Reichsanstalt. The switch S for closing and opening the current served for measuring off the time. Fig. 6

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[1]) In the figure the regulating resistance and the milli-ampèremeter between accumulator and commutator have been omitted.

represents the complete arrangement[1]) for measuring off and registering the time. The clock U with second pendulum, provided with a Hohwü registering arrangement H, closes, respectively

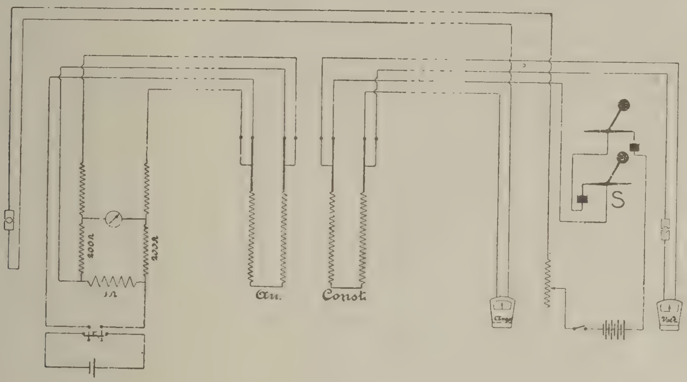

Fig. 5.

opens in passing its equilibrium position a current which operates a relais Q. This closes, respectively opens a current, which makes the bell L give a stroke every two seconds; this is registered by the telegraphic apparatus T the Morse-key M being in its position

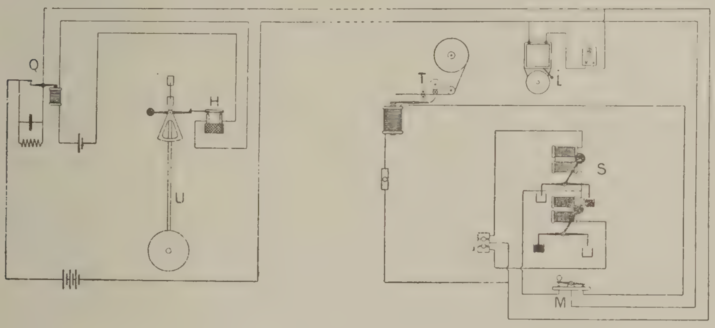

Fig. 6.

of rest. If, after contact has been made at i by a plug, M is pressed down at a moment that no current goes through (to be recognized from the position of the tongue of the bell), at the next closing of the current by the relais the beam j_i of the contact-key S_i (see Fig. 7) will be released, the platinum wire p_{i_2} will fall into the mercury, and the heating current through the constantin wire will be closed[1]. The switching out is operated in the same way by S_u the contact plug having been transferred from i to u. As a control the moments of switching in and out are registered by T (Fig. 6) through the corresponding dash on the paper strip being absent.

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[1]) This arrangement was already used in the determination of the heat of vaporisation of hydrogen, cf. Comm. N⁰. 137*e*.

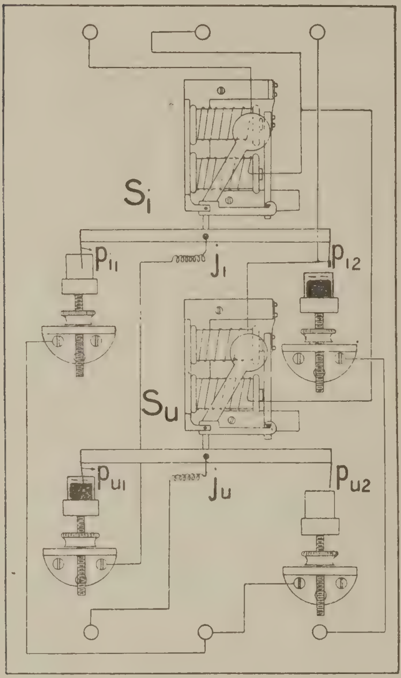

Fig. 7.

An accuracy of $^1/_{10}$ of a second is certainly attained with this arrangement.

The temperature measurement. The scale of the gold resistance thermometer is dealt with in § 3. In Fig. 6 the Thomson bridge for the measurement of the resistance is also represented. The galvanometer was of the Diesselhorst type with a period (undamped) of 4 sec. Before a calorimetric determination the resistance was measured, and the deflection of the galvanometer for a definite change in the ratio of the branches in the Thomson bridge, the "sensitivity", determined. Then with a definite ratio of the branches the movement of the galvanometer (Fig. 3 and 4) was followed during the experiment. After this the measurements of the resistance and of the sensitivity were repeated. The current for measuring the resistance was 5 milliampères. The heating current was for the lead 30 to 50, for the copper 12 to 27 milliampères. Considering the ratio between the resistances of the thermometer and the heating wires the development of heat in the temperature measurement does not come into account.

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[1] The distances of the points of p_{i_2} and p_{u_1} (fig. 7) above and below the respective mercury surfaces (covered with paraffin oil partly for suppressing the opening spark) are small and are made equal to each other by adjusting the mercury cups, whereas the velocity of fall of the two beams j_i and j_u was also made as equal as possible. The two other cups (see p_{i_1} and p_{u_2}) may serve to use the apparatus as a switch-over key (e.g. if the same wire has to be used as a heating and as a thermometer wire, cf. § 3 at the end); in the present experiments they were not filled with mercury.

We gladly record our cordial thanks to Dr. G. HOLST and Mr. P. G. CATH for the aid they afforded us in undertaking the temperature measurements.

Account had to be taken of the circumstance, that the reduction factor, which gives the ratio between the galvanometer current in the THOMSON bridge and the difference between the measured resistance and the resistance which would give no deflection, depends on the resistance in the variable branches of the bridge. A correction for this was always applied.

§ 3. *The resistance thermometer.* For the resistance thermometer a gold wire was chosen, as in the range of the measurements (14—90° K.) gold is more suitable for interpolation than platinum [1]), and as on the other hand the indications of the gold thermometer are constant [2]), if it is suitably treated before use (glowing before winding, then repeatedly cooling in liquid hydrogen and returning to room temperature). Before each series of measurements the constancy of the wire was tested by a measurement at the boiling point of hydrogen.

In the temperature range of liquid hydrogen the gold thermometer was calibrated with the aid of a hydrogen vapour pressure apparatus as used in Comm. N⁰. 137*d*. The temperatures were deduced from formula (1) of that paper In this way the scale of the gold thermometer is reduced to that of $Pt_{I'}$ which has been once more accurately fixed by the research of KAMERLINGH ONNES and HOLST

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[1]) H. KAMERLINGH ONNES and G. HOLST. Comm. N⁰. 142*a* (June 1914).

[2]) At least if the wire is mounted in such a way that it can expand and contract freely, as was e. g. the case with Pt_I. Later experience (cf. Comm. N⁰. 147*a* § 1) has shown that at the liquid hydrogen temperatures a gold thermometer which is inclosed in enamel between metal shows small variations. [Note added in the translation].

(Comm N⁰. 141*a*). In the range of liquid oxygen this was done with the aid of auxiliary thermometers of platinum and of gold which had been compared directly with Pt_P.

The data for the gold thermometer Au_{c_1} 1)), which was used in the measurements of May—June 1913 (table IV), were inserted in Comm. N⁰. 142*a* § 4*e*. Table I contains the data for the gold thermometer Au_{c3}, which was used in June—July 1914 2)).

TABLE I.

No.		T	Resistance of Au_{c_3} 3))			Resistance of constantin $Const._{c_3}$
				W-R_I	W-R_{II}	
May 23 '14.	I	14.16°K.	0.6148	0.00	0.00	136.621
	II	15.79	6286	— 10	+ 1	918
	III	17.00	6419	— 14	0	137.138
	IV	17.96	6542	— 14	0	312
	V	19.35	6749	— 8	0	565
	VI	20.31	6911	0	0	743
May 20		20.48	6946	— 0^5	— 3	776
May 18	III	68.22 4))	2.6093			143.388
	IV	78.28	3.0917			144.000
	I	90.27	3.6549			656
May 25 5))		90.45	3.6616			

We also communicate in table II the calibration data of a gold

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1) Wire of 0.05 mm. of Heraeus.

2) Cf. Comm. N⁰. 147*a*, for later calibrations. [Added in the translation].

3) Wire of 0.1 mm. furnished in January 1914 by Heraeus.

4) Cf. note 1, p. 20. [Added in the translation].

5) This measurement, which was used to conclude that the gold thermometer after having been immersed in liquid hydrogen had not changed, was not mentioned in the edition of this paper in the Academy. [Added in the translation].

thermometer Au_{c2}, which became defective in some measurements concerning the specific heat of aluminium.

In connection with a remark by ZERNIKE in a paper published in these Proceedings, viz. that the resistance of Au_{c1} (Comm. N⁰. 142*a* § 4*e*) for the range of hydrogen temperatures can be represented fairly accurately by a formula

$$W = a + b\,T^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

we have inserted under $W - R_I$ in the tables I and II the differences between the observed temperatures and those calculated from the resistances with the formulae:

$$W = 0.5912 + 5.871 . 10^{-7} . T^4 \qquad (Au_{c3}) \quad . \quad . \quad (2a)$$

$$W = 0.07279 + 1.0974 . 10^{-7} . T^4 \qquad (Au_{c2}) \quad . \quad . \quad (2b)$$

TABLE II.

Resistance of Au_{c2} [1])

No.	T	Resistance	$W - R_I$	
	In liquid hydrogen with vapour pressure apparatus			
Dec. 9 '13 II	14.25	0.07731^5	0.00	
III	14.95	7831	— 3	
IV	16.02	8019	— 9	
V	17.05	8232	— 12	
VI	18.01	8461	— 11	
Dec. 8 I	18.04	8466	— 9^5	
,, 9 VII*a*	19.36	8838	— 5	much liquid in vapour pressure apparat.
b	19.36^5	8839^5	— 5^5	little ,,
VIII	20.36	9165	0	
	in liquid oxygen with $Pt_{I'}$			
Dec. 16 IV	59.00	0.4392		
III	77.84	6552		
,, 15 II	86.41	7517		
,, 16 II	86.43	7519		
,, 15 I	90.20	7941		
,, 16 I	90.30	7962		

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[1]) Wire of 0.1 mm. of HERAEUS.

In Fig. 8 we have represented besides these deviations (indicated by squares and triangles respectively), also those of Au_{c_1} (indicated by circles), for which T was calculated from

$$W = 0.2691 + 5.425 \,.\, 10^{-7}\, T^4 \qquad (Au_{c_1}) \quad . \quad . \quad (2c)$$

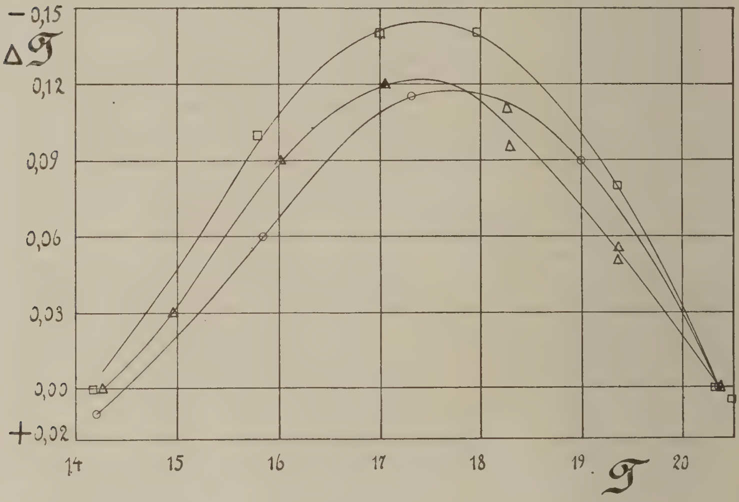

Fig. 8.

These deviations are certainly not large (at most rather more than 0.1 degree); they are, however, appreciably larger than the inaccuracy of the measurements. They are on the whole larger as the impurity of the wire $\left(\text{as estimated by the ratio } \frac{a}{b}\right)$ increases. This increase of the deviations with increasing impurity seems, however, not to be strong enough to warrant the conclusion, that for pure gold proportionality of the resistance with T^4 within the limits of the accuracy of the measurements would exist in the hydrogen region. This will find its expression in Zernike's more general interpolation formula in the fact, that in this range the coefficients of the polynomial in the denominator already make their influence felt. Grüneisen's relation $W \sim C_p\, T$ brings this in connection with the deviation which the specific heat of gold shows in this range from the T^3-law [1]).

In table I under $W - R_{II}$ we have also inserted the deviations between the observed temperatures and those calculated from the formula:

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[1]) 8% at 20° K. if for gold $\Theta = 166$ is assumed according to Debije.

$$W = 0.6879 - 0.01741\, T + 0.000865\, T^2. \qquad (Au_{c3}) \quad . \quad (3)$$

Practically this formula represents the resistance of Au_{c3} accurately in this range so that in the hydrogen range dW/dT depends linearly on T. Outside this range the formula would lead, however, to quite incorrect values [1]).

For the calculation of the results of the calorimetric determinations dealt with in this paper graphic interpolation was made use of. For the hydrogen range graphs of W and of $\Delta W/\Delta T$ were made on a sufficiently large scale according to the observed values. For the higher temperatures T and dW/dT were taken from graphs for the whole range of the calibration; for that purpose the W-curve was first drawn, from this values of dW/dT were taken for a number of points in the range between hydrogen and oxygen temperatures, and these values were then smoothed graphically in the dW/dT-figure.

Together with the gold wire we accurately calibrated each time the constantin wire which was to serve for the heating, in order that this wire might serve as thermometer also (cf. p. 10 note 1) in case the gold wire should become defective. The corresponding data are given in Comm. N^0. 142*a* § 4*d* and in this paper table I.

§ 4. *Heat capacity of the core.* This was measured separately in the same way as described in the preceding §§ for the block of metal and core together. We only communicate the results of the measurements for the core K_{III} which served for the measurements of June/July 1914 (table III).

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[1]) We have also investigated whether the resistances of Au_{c_3} and Au_{c_1} (of which the first mentioned was enclosed in enamel, the second in paraffin) can be reduced to each other, either with the linear relation, which according to NERNST from 56 to 273° K., or with the quadratic one, which according to HENNING from 80 to 273° K. exists between the values of the resistances of platinum wires corresponding to the same temperature. We found, however, that in the range from 14° to 90° K. both relations give deviations of several tenths of a degree between calculation and observation. The same result as regards NERNST's rule was found recently by H. SCHIMANK, Ann. d. Phys. (4) 45 (1914), p. 706. As regards the exceptional difference which was found by this physicist between observation and calculation in the case of Au_{VI} (Comm. N^0. 99*b* by KAMERLINGH ONNES and CLAY), we refer to the erratum given in Suppl. N^0. 19 (May 1908): in Comm. No. 99*c* p. 22 table I column Au_{VI} for 0.16822 is to be read 0.25234.

TABLE III.

Heat capacity of the core K_{III}			
No.	Mean temperature	Increase of temperature	Heat capacity in Joules / degree K.
June 10 II	14.61° K.	0.763	0.727
III	15.28	1.123	0.785
IV	16.19	0.992	0.887
V	17.37	1.149	1.019
VI	18.28^5	0.964	1.155
VII	19.11^5	0.867	1.288
I	20.10^5	1.288	1.530
VIII	20.16	1.048	1.406
IX	21.13	0.938	1.565
X*)	28.37^5	0.979	2.99
XI*	29.00	0.927	3.17
XII	36.40	0.675	5.04
XIII*	46.32	0.509	8.19
June 13 II*	61.87	0.503	12.91
III*	62.16	0.490	13.22
IV	70.33	0.429	15.39
V	70.74^5	0.417	15.58
I*	80.36	0.346	18.74
June 14 I	80.51^5	0.318	17.87
II	80.88	0.356	18.56

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1) For the measurements marked by an * the calculation of the increase of temperature was not based on the determinations of the sensitivity (§ 2) immediately before and after those measurements, as in this case irregularities appeared to have occurred which have not yet been explained, but on an average value of the sensitivity, which was deduced for a number of successive measurements to which these belong. Apart from these irregularities the individual values for the sensitivity in one series of measurements did not differ as a rule by more than 2 to 4% (occasionally by 6%). [For new measurements of the heat capacity of K_{III} cf. Comm. No 147*a*. Added in the translation].

§ 5. *Lead.* With lead ("KAHLBAUM") 3 series of measurements were made. The results of the first two series (1913) have been united in table IV, that of the last series (1914) in table V. Weight of the lead block: for the measurements of table IV: 715.6 grammes, for those of table V (the same block after removal of a layer at the surface) 709.6 grammes.

The measurements of 1914 must be considered as more accurate than those of 1913. Nevertheless the latter are also communicated, as they confirm the conclusions to be drawn from the others.

C_v was derived from C_p with the aid of the relation given by NERNST [1]) for lead:

$$C_p - C_v = 3{,}2 \,.\, 10^{-5}\, T\, C_p^2.$$

TABLE IV.

Atomic heat of lead.

No.	Mean temperature	Increase of temperature	Heat capacity block + core in Joules/degree K	id. core	Atomic heat in cal$_{15}$/degree K. $C_p = C_v$
May 16 '13 II	14.96° K.	0.66	23.79	0.28	1.62
III	15.86	0.73^5	27.27	0.33	1.86
IV	16 62^5	0.67	29.75	0.37	2.03
V	17.38	0 81	31.37	0.42	2.14
VI	18.19	0.73^5	33.85	0.49	2.30
VII	18.98	0.84^5	35.46	0.58	2.41
VIII	19.81	0.80^5	37.20	0.69	2.52
June 5 '13 I	15.00	0.73^5	24.73	0.29	1.69
II	15.71	0.79^5	27.11	0.32	1.85
III	16.43	0.71	30.37	0.36	2.07
IV	17.22	0.84	31.58	0.41	2.15
V	18.16	0.78	34.73	0.49	2.36
VI	19.10	0.95	36.68	0.59	2.49
VII	20.10^5	0.95	36.78	0.74	2.49

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[1]) W. NERNST, Ann d. Phys. (4) 36 (1914), p. 426.

In fig. 9 C_v is represented according to the observations of 1914; fig. 10 gives a representation for the range of the hydrogen temperatures separately, the observations of 1913 (ΔΔ and ∇∇) being also included.

TABLE V.

Atomic heat of lead.

No.	Mean temperature	Increase of temperature	Heat capacity lead block + core in Joules/degree K.	Atomic heat in cal.$_{15}$/degree K.		Θ
				C_p	C_v	
June 23 '14 XIV	14.19° K.	1.106	23.08	1.56	1.56	85.7
III	15.31^5	0.927	26.83	1.81^5	1.81^5	85.9
IV	16.27^5	0.980^5	29.42	1.99	1.99	86.6
V	17.24	1.001	32.18	2.17	2.17	86.9
VI	18.25^5	1.008	35.72	2.41	2.41	86.3
VII	19.27	1.054	37.56	2.53	2.53	88.2
VIII	20.30^5	1.073	39.57	2.66	2.66	89.5
II	22.31	0.962	44.58	2.98	2.97	89.9
IX	27.51	1.019	54.41	3.60	3.59	92.4
X	28.50	0.993	55.52	3.66	3.65	94.0^5
XI	36.49^5	1.061	69.33	4.47	4.45	90.5
XII	45.61^5	0.469	77.53	4.85	4.81	
XIII	46.25	0.907	80.50	5.04	5.00	87.9
June 24 I	57.20	0.476	89.47	5.43	5.38	
II	58.00	0.804	88.93	5.37	5.32	88.5
III	69.28	0.676	92.19	5.37	5.31	
IV	69.97	0.723	92.82	5.40	5.34	
V*1)	80.36^5	0.661	101.07	5.77	5.70	
VI*	80.86^5	0.671	99.82	5.67	5.60	90.1

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1) Cf. note 1, p. 16.

In these figures the curve, which according to DEBIJE represents the atomic heat, calculated with $\Theta = 88$, which value was also derived by EUCKEN and SCHWERS from their measurements on lead, is represented too. In agreement with EUCKEN and SCHWERS we find that the observations show a good concordance with DEBIJE's formula over the whole range. This concordance is, however, not complete; deviations show themselves which exceed the uncertainty of the results of the observations [1]). This appears to be the case in the first place in the range of hydrogen temperatures: the curve which unites the experimental results crosses the curve calculated according to DEBIJE (Fig. 10), in such a way that at 14° K the specific heat is greater, at 20° K. it is smaller than the value calculated with $\Theta = 88$. These deviations continue in the lower part of the range between hydrogen and oxygen temperatures, and decrease

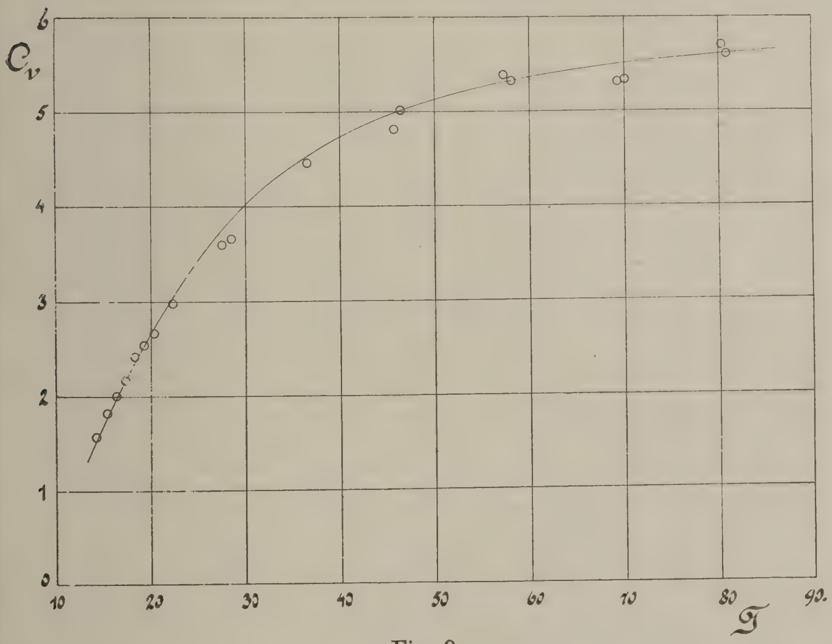

Fig. 9.

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[1]) At the points $T = 57.20$, 69.28 and 69.97 the irregularities mentioned in note 1 p. 16 in the determination of the sensitivity have presumably also occurred, though in a less degree. The first point has probably been calculated with too large, the last two with too small a value for the sensitivity.

again in the higher part. It is true that the drawing of a conclusion is made uncertain in this region by the interpolation, which the gold thermometer requires there [1]). We do not, however, consider it probable, that the deviations in this region are to be ascribed to the inaccuracy of the interpolation: 1. as they are a regular continuation of the deviation of the hydrogen region which are established with certainty, 2. as there are no indications that the deviations have a different sign in one part of the region of interpolation than in the other, as would have been the consequence of an inaccurate interpolation with the method of interpolation used (§ 3).

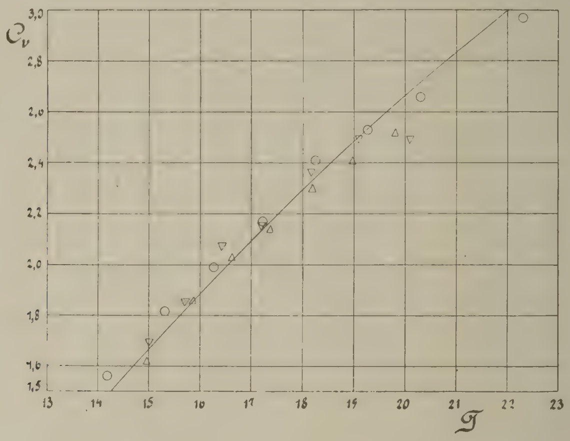

Fig. 10.

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[1]) Our conclusions concerning the region between liquid hydrogen and liquid oxygen temperatures have since become somewhat more uncertain as in later calibrations of Au_{c_3} (cf. Comm. N⁰. 147*a*) it has appeared that the point $T = 68.22$ in table I is not very accurate. A correction for this has an appreciable influence only on the value of C_v for $T = 36.49^5$. The corrected point in the C_v -diagram lies a little *above* the DEBIJE curve so that as arguments for the deviations from DEBIJE'S formula in the considered region only the determinations at 28°—19° K. remain. As the apparatus allow to obtain a greater accuracy now, a new series of measurements on lead seems desirable. In this respect it is also important that by the arrangement of the neon cyclus and the construction of cryostats for temperatures between those of liquid hydrogen and liquid oxygen (Comm. N⁰. 147*c*, June 1915) thermometer calibrations in this region have become possible. [Note added in the translation].

We are therefore led to the conclusion that the specific heat of lead shows deviations from the curve calculated according to DEBIJE, which unites the determinations at oxygen and at hydrogen temperatures in the best possible way ($\Theta = 88$), in the intermediate range of the temperatures, to the extent of about 4 % at 30° K. (cf. also table VI).

These deviations may presumably find their explanation in one or more of the following circumstances: *a*. that we did not observe with a homogeneous substance crystallized in the regular system, but with a micro-crystalline aggregate consisting of different phases, such as the two different states of crystallisation assumed in supraconductors for the explanation of the micro-residual resistance (Comm. N⁰. 133 § 11), which perhaps also come into play in the experiments of COHEN and HELDERMAN [1]), who on the ground of their investigations assume, that with lead we are dealing with a metastable complex of two or more modifications, *b*. that the approximate suppositions concerning the elastic spectrum made in DEBIJE's theory are not strictly valid, *c*. in a change with the temperature of the quantity Θ which occurs in that theory, in other words of the elastic properties of the material [2]).

Cornerning *b* it may be remarked that for a substance which should crystallize in the simplest cubical space-lattice THIRRING has derived an expression for the specific heat from the theory of BORN and v. KÁRMÁN which in consequence of the more rigorous consideration of the molecular structure followed in this theory might give a nearer approximation to the actual conditions. It is true that for a thorough discussion in connection with THIRRING's deductions the data about the elastic constants in the temperature region considered are as yet wanting. Without these we can, however, establish the following facts.

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[1]) E. COHEN, Proc. Kon. Akad. Amsterdam June 1914, p. 200; E. COHEN and W. D. HELDERMAN, Proc. Kon. Akad. Amsterdam Nov. '14 p. 822. COHEN l.c. quotes measurements of LE VERRIER according to which at 220 to 250° C. lead would pass into another modification with appreciably larger specific heat (at constant pressure). The measurements by P. SCHÜBEL, ZS. f. anorg. Chem. 87 (1914), p. 81, do not, however, confirm this result.

[2]) In determining this influence it should be borne in mind that, as is specially pointed out by EUCKEN, Verh. d. D. physik. Ges. 15 (1913), p. 571, the elastic properties must have been measured on homogeneous crystalline material.

TABLE VI.

T	C_v	$W-R_D$ $(\Theta = 88)$	$W-R_{Th_1}$ $(\Theta_{Th1}=67.5)$	$W-R_{Th_2}$ $(\Theta_{Th_2}=68)$
14.19	1.56	+ 0.08^5		
15.31^5	1.81^5	+ 8^5		
16.27^5	1.99	+ 6		
17.24	2.17	+ 5	+ 0.26	
18.25^5	2.41	+ 8	+ 28	
19.27	2.53	0	+ 19	
20.30^5	2.66	− 7	+ 11	
22.31	2 97	− 7^5	+ 4	
27.51	3.59	− 15	− 10	
28.50	3.65	− 20	− 16	− 0 20
36.49^5	4.45	− 8	− 7	− 7
46.25	5 00	0	0	+ 1
58.00	5.32	− 1	− 1	− 1

In table VI are given besides the deviations ($W-R_D$) between the observed values of C_v and those calculated according to DEBIJE with $\Theta = 88$, also the deviations $W-R_{Th_1}$, between the observations and the values calculated from a series given by THIRRING:

$$C_v = 3R\left\{1 - \frac{B_2}{2!}\left(\frac{\Theta_{Th}}{T}\right)^2 + 3\frac{B_4}{4!}\left(\frac{\Theta_{Th}}{T}\right)^4 - 5\frac{B_6}{6!}\left(\frac{\Theta_{Th}}{T}\right)^6 \ldots\right\} \quad . \; . \; (4)$$

in which $B_1, B_2 \ldots$ are the Bernouillian coefficients and Θ_{Th} is a constant. Apparently the agreement of the observations with DEBIJE's formula is closer than that with this series of THIRRING.

It deserves further to be noticed, that this series can only be derived from the theory of BORN and v. KÁRMÁN by the introduction of imaginary values for the elastic constants (assuming that they are independent of the temperature). From the series which THIRRING derives from the theory mentioned above:

$$C_v = 3R\left\{1 - \frac{B_2}{2!} J_1 \left(\frac{h}{kT}\right)^2 + 3\frac{B_4}{4!} J_2 \left(\frac{h}{kT}\right)^4 \ldots\right\} \quad . \; . \; . \; . \; (5)$$

where $J_1, J_2 \ldots J_4$ represent definite functions [1]) of the elastic constants c_{11}, c_{44}, c_{12} introduced by VOIGT, the following series may be derived as the one which at the higher temperatures approaches nearest to series (4) [2]):

$$C_v = 3R \left\{ 1 - \frac{B_2}{2!}\left(\frac{\Theta_{\mathrm{Th}}}{T}\right)^2 + 1.1 \cdot 3\,\frac{B_4}{4!}\left(\frac{\Theta_{\mathrm{Th}}}{T}\right)^4 - 1.278 \cdot 5\,\frac{B_6}{6!}\left(\frac{\Theta_{\mathrm{Th}}}{T}\right)^6 + 1.6393 \cdot 7\,\frac{B_8}{8!}\left(\frac{\Theta_{\mathrm{Th}}}{T}\right)^8 \ldots \right\} \quad \ldots \quad (6)$$

Under $W—R_{\mathrm{Th}2}$ in table VI are given the deviations between the observations and the values calculated from (6) with $\Theta_{\mathrm{Th}2} = 68$. It appears that THIRRING's formula (5) with the special assumptions concerning the elastic constants for which it passes into (6), in the region for which the coefficients have been developed by him, practically coincides with DEBIJE's formula. Whereas, when the elastic constants do not agree with those assumptions, THIRRING's formula deviates from DEBIJE's formula in a direction opposite to the observations.

Hence we come to the conclusion that a closer consideration of the molecular structure in the sense in which it is done in the theories of BORN and v. KÁRMÁN and of THIRRING, at least on the assumption of the arrangement in the simplest cubic space-lattice, does not account for the deviations indicated above.

It remains either to consider an arrangement in one of the other space-lattices of the regular system [3]), or to assume that one or both of the circumstances mentioned above under *a* and *c* also play a part [4]). The latter of these, viz a change of the elastic properties with the temperature, would be connected with deviations from the linear relation between the forces between the molecules and their relative displacements, which deviations DEBIJE [1]) also makes responsible for the thermal expansion.

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[1]) H. THIRRING. Physik. Z.S. 14 (1913), p. 870 and 15 (1914), p. 181 note 1.

[2]) This would require $c_{11} = \frac{3}{2}\, c_{44}$, $c_{12} = 0$.

[3]) A comparison with the deduction by BORN, Ann. d. Phys (4) 44 (1914), p. 607, of C_v for the space-lattice as deduced by BRAGG for diamond (also a regular crystal) leads, however, to quite analogous results as are given above for the simplest cubic space-lattice.

[4]) Regarding *a* it may still be remarked that the presence of a second modification of appreciably different properties in a considerable quantity would lead us to expect much larger deviations from DEBIJE's formula than appear actually to exist. If the circumstance mentioned under *a* plays a part, we therefore have to assume a small quantity of a second modification, or a second modification whose elastic properties are only little different from those of the first.

In table V are given the values of Θ, which are obtained by applying DEBIJE's formula for C_v to the individual observations. They are united in Fig. 11 [2]) [3]).

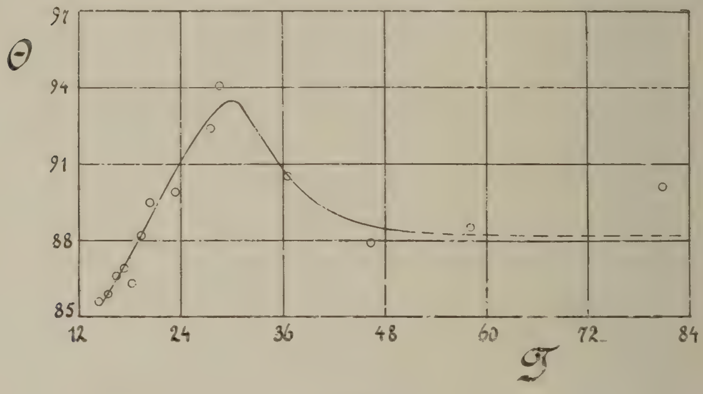

Fig. 11.

§ 6. *Copper.* With copper we were as yet only able to make a series of measurements between 15 and 22° K. The copper was electrolytic copper of FELTEN and GUILLAUME, 596,0 grammes.

$\overline{C}_p$ in table VII represents the mean atomic heat between the initial and final temperatures; for correction to the "true" atomic heat $C_p = C_v$ corresponding to the mean temperature of the measurement use was made of the proportionality $C_v \sim T^3$, which appears to be valid in this region.

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[1]) P. DEBIJE Vorträge Wolfskehlcongres Göttingen 1913.

[2]) The slow change, which EUCKEN and SCHWERS l.c. observed in the values of Θ for lead as derived from their measurements, and which is considered by them as probably due to the uncertainty of the temperature coefficient of their resistance thermometer, does not coincide with that found by us.

[3]) Fig. 11 gives a special illustration of the character of the deviations from DEBIJE's formula over the whole range, and can also serve to calculate a smoothed value of C_v by reading the value of Θ corresponding to a definite T from the smoothed curve. At the same time it should be remarked, that the values of Θ represented in Fig. 11 do not coincide with $h\nu_{\max}/k$, if $\nu_{\max}$, the maximum frequency according to DEBIJE, changes with T.

TABLE VII.

Atomic heat of copper.

No.	mean temp.	increase of temperature	heat capacity copperblock + core in Joules/degree K.	Atomic heat in cal$_{15}$ / degree K.	
				$\overline{C}_p$	$C_p = C_v$
July 3 '14					
II	15.24° K.	4.222	2.748	0.0500	0.0491
III	17.50	0.920	3.895	726	726
IV	18.03	0.842	4.222	792	792
V	18.89	0.726	4.884	930	930
VI	19.58	0.606	5.305	1010	1010
VII	20.88	1.355	6.417	1248	1247
I	21.50^5	2.156	7.159	1414	1410

Table VIII contains the comparison of the experimental values with the relation given by DEBIJE for sufficiently low temperatures:

$$C_v = 77.94 \cdot 3\,R\left(\frac{T}{\Theta}\right)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

TABLE VIII.

Atomic heat of copper.

T	C_v	Θ	$C_v$calc. ($\Theta = 323.5$)	Obs.—Calc.	
					in %
15.24	0.0491	322.3	0.0486	+ 0.0005	+ 1.0
17.50	726	324.9	735	— 9	— 1.2
18.03	792	325.2	804	— 12	— 1.5
18.89	930	322.9	925	+ 5	+ 0.5
19.58	1010	325.6	1030	— 20	— 1.9
20.88	1247	323.7	1249	— 2	— 0.2
21.50^5	1410	320.0	1365	+ 45	+ 3.3
		mean 323.5			

The column headed Θ contains the values of Θ calculated according to formula (7) from the individual measurements.

From these measurements the conclusion can be drawn, that in the temperature range from 15 to 22° K. the specific heat of copper follows DEBIJE's law within 2 % [1]).

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[1]) Later, more accurate measurements (cf. Comm. N⁰. 147*a*) show that in this region a small deviation from the T^3-law exists which slightly surpasses the amount mentioned above. [Added in the translation].

Errata Communication N⁰. 144.

p. 7 line 11 from the top: for „collonnes” read „colonnes”.

p. 46 in the formula: for „$B_t \frac{p_t}{76} \frac{1}{1 + \frac{t}{273}}$” read „$\left(B_t \frac{p_t}{76}\right)^2 \frac{1}{1 + \frac{t}{273}}$”

p. 56 line 4 from the bottom: for „10^{-6}” read „10^{-5}”.

Erratum Comm. No. 144.

p. 57 line 6 from the top: for „222.4 10^{-6}” read „222.4 10^{-5}”.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

N°. 144ª.

H. KAMERLINGH ONNES. Organisation des expériences sur les propriétés thermodynamiques de l'ammoniaque et du chlorure de méthyle.

(*Translated from: Notes on the Work of the Section for physics, chemistry and thermometry of the first international commission of the Association Internationale du Froid, presented at Third International Congress of Refrigeration, Washington-Chicago* **Sept. 15** *to* **Oct. 1, 1913**).

Eduard IJdo — Printer — Leiden.

H. KAMERLINGH ONNES. *Organisation des expériences sur les propriétés thermodynamiques de l'ammoniaque et du chlorure de méthyle.*

NOTES ON THE WORK OF THE SECTION FOR PHYSICS, CHEMISTRY AND THERMOMETRY OF THE FIRST INTERNATIONAL COMMISSION OF THE ASSOCIATION INTERNATIONALE DU FROID.

III

NOTE

PRÉSENTÉE À LA COMMISSION PRÉPARATOIRE
pour
L'ÉTUDE DES GAZ FACILEMENT LIQUÉFIABLES
composée de
MM. J. E. BUCKINGHAM (Etats-Unis), H. C. DICKINSON (Etats-Unis), C. DIETERICI (Allemagne), A. W. GRAY (Etats-Unis),
E. MATHIAS (France), J. P. KUENEN (Pays-Bas),
H. KAMERLINGH ONNES (Pays-Bas), R. MOLLIER (Allemagne),
SYDNEY YOUNG (Angleterre), S. W. STRATTON (Etats-Unis),
J. E. VERSCHAFFELT (Belgique);
par
H. KAMERLINGH ONNES.

§ 1. *Utilité de ces recherches.*

Lors des congrès du froid les ingénieurs [1]) ont insisté, à différentes reprises, sur l'utilité de nouvelles déterminations des propriétés thermodynamiques des gaz employés dans l'industrie frigorifique et spécialement de l'ammoniaque et du chlorure de méthyle.

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[1]) Voir e. a. J. C. BERTSCH, ZS. Eis u. Kälte-Ind. 1913, 139; J. E. STARR, Ice and Refrig. 1912, 125, 352. J, HYBL, ZS. Eis und Kälte-Ind. 1913, 120, etc.

Un certain nombre d'auteurs et spécialement Mollier, dont les diagrammes sont bien connus, ont établi des courbes et des tableaux permettant l'emploi immédiat des caractéristiques de ces agents frigorifiques pour l'étude de la construction rationelle des installations frigorifiques.

Le besoin d'une base expérimentale, suffisamment précise, se fait sentir lorsque l'on arrive au calcul des tables nécessaires pour la construction de ces graphiques.

Il n'y a pas très longtemps que la situation était d'ailleurs la même pour le plus important de tous les gaz industriels: la vapeur d'eau. Les travaux précis de ces dernières années nous ont donné à cet égard une excellente base de déterminations. Or, parmi les gaz liquéfiés, l'ammoniaque et le chlorure de méthyle se présentent tout particulièrement dans de mauvaises conditions. Pour l'anhydride sulfureux et l'acide carbonique, il y a eu beaucoup de déterminations et il semble, notamment pour l'acide carbonique, que l'on peut établir avec les différentes données que nous possédons actuellement des graphiques très satisfaisants en introduisant dans ces calculs l'équation d'état qui a été déduite des observations très précises d'Amagat, par la méthode des polynomes 1). Pour l'ammoniaque, un essai de détermination des constantes nécessaires a été réalisé, mais, comme on le verra dans la Note IV 2), presque la moitié de la meilleure table que nous possédons a été établie par extrapolation. Pour l'autre gaz, le chlorure de méthyle, c'est à peine si nous possédons une ou deux déterminations.

§ 2. *Limite des recherches.*

Il me semblait qu'une amélioration très urgente pourrait être apportée aux bases physiques de l'industrie frigorifique par des recherches ayant en vue de completer, pour l'ammoniaque et le chlorure de méthyle, les données déjà acquises dans la mesure où celles-ci peuvent être considérées comme ayant une exactitude suffisante, pour la construction du diagramme thermique, avec une précision de $^1/_2$ pour cent, et des isothermes, avec une précision

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1) H. Kamerlingh Onnes. Communications from the Physical Laboratory of Leiden N°. 74.

2) Comm. N°. 144*b*.

de $^1/_5$ pour cent, en les étendant à toute l'échelle de température utile pour l'industrie frigorifique. Nous aurons alors une base suffisamment digne de confiance pour la construction des installations frigorifiques et, en même temps, un bon guide pour notre Commission préparatoire lorsqu'elle arrivera à envisager le problème de la détermination des propriétés thermodynamiques de ces gaz, sur une plus large échelle, ou avec un plus grand degré d'exactitude, c'est-à-dire, en somme, arriver sous ce rapport à une exactitude égale à celle du diagramme thermique de la vapeur d'eau. M. G. HOLST a entrepris des recherches sur la base que nous venons d'indiquer. Nous verrons au § 4 que ce travail a pu être organisé de façon que, en ce qui concerne les propriétés thermiques des vapeurs surchauffées, une précision finale, égale à celle du diagramme de la vapeur d'eau, pouvait être obtenue, car ces propriétés ont pu être déterminées pour toute la région couverte par les expériences avec une exactitude suffisante, même si la haute précision du diagramme de la vapeur d'eau est prise comme unité de précision. Nous avons fait de notre mieux pour organiser ces expériences de telle façon que ce qui était le plus urgent soit fait en premier et nous nous sommes abstenus de l'étude des très basses températures, bien que celle-ci soit de plus en plus demandée dans l'avenir par les industries chimiques. Nous avons pris — 40° C. comme limite inférieure de température et + 40° C. comme limite supérieure de température intéressante pour les vapeurs saturées. Cette limite est beaucoup plus haute pour les vapeurs surchauffées et, la surchauffe étant employée dans de nombreux cas nous avons été obligés d'envisager ceux-ci, mais il me semble que + 100° C. marquent une limite au-delà de laquelle il est inutile d'aller.

Les pressions sont prises, pour l'ammoniaque, entre $1^1/_2$ atmosphères et 15 atmosphères et, pour le chlorure de méthyle, entre 1 et 8 atmosphères.

§ 3. *Discussion des données actuelles* [1].

Au centre de cette discussion se place le théorème des états correspondants et les petites déviations des substances considerées, de cette loi, ont fait le sujet de nos recherches. On fait usage dans les calculs de l'équation d'état empirique générale moyenne [1]), l'équation d'état réduite pour ainsi dire d'une substance fictive, qui est pour le domaine considéré de températures réduites approximativement la moyenne des équations réduites de l'éther et de l'isopentane.

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[1] Au moment d'envoyer cette note à l'impression, j'ai reçu une communication de MM. GOODENOUGH et MOSHER sur les propriétés de la vapeur d'ammoniaque saturée et surchauffée, où une autre discussion complète et minutieuse

Pour les vapeurs surchauffées, on a fait usage du développement de l'équation moyenne réduite en un polynome de puissances de la densité réduite avec, comme coefficients, des fonctions de la température, nommées coefficients viriels, qui sont encore développées sous la forme d'un polynome de puissances de la température réduite. Les différences entre ces coefficients et les coefficients de la substance considérée qui en sont un peu différentes sont discutées. Dans le cas de densités de liquides, le diamètre de la substance expérimentée n'ayant pas encore été calculé, on le suppose presque égal à la moyenne de l'isopentane et de l'éther. Les diamètres réduits de l'ammoniaque et du chlorure de méthyle sont donc comparés immédiatement avec ceux de l'isopentane et de l'éther, comme il a été expliqué par M. Holst dans la note IV.

La méthode de l'équation d'état moyenne réduite se montre encore dans ces calculs un moyen excellent de discuter les différentes données expérimentales relatives à la même propriété d'une substance qui dépend de deux variables indépendants.

La discussion des différentes observations sur les pressions de vapeur a été faite directement, sans l'intermédiaire de la loi des états correspondants, car là, un seul variable indépendant entre en jeu.

Il n'y a pas de données suffisantes pour permettre la discussion de la chaleur spécifique à l'aide de la relation entre la chaleur spécifique du liquide et celle de la vapeur, et permettre le calcul de l'une tirée de l'autre, quand l'équation d'état est connue.

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des données existantes pour l'ammoniaque — en ce qui concerne la pression de sa vapeur en comparaison avec celle de l'eau — est faite et où les tables et les graphiques pour cet agent sont calculés sur la base de ces données. Les auteurs, dans l'introduction de leur travail, font remarquer que l'achèvement du travail expérimental est particulièrement désirable et que les valeurs tabulaires qu'ils donnent ne doivent pas être considérées comme définitives.

[1]) H. Kamerlingh Onnes. Communications de Leyde, nos. 71, 74.

Une vérification de la valeur des différentes données a été obtenue en calculant la chaleur latente de vaporisation, d'après les tensions de vapeur observées, et l'équation d'état, par la formule de CLAPEYRON, et en les comparant à la valeur déduite des expériences.

§ 4. *Les moyens expérimentaux.*

Au Laboratoire de Leyde, nous avions à notre disposition des moyens immédiatement appropriés pour l'exécution des travaux projetés.

En premier lieu, nous avions le manomètre absolu, donnant la pression par lecture directe des collonnes de mercure [1]), jusqu'à une pression beaucoup plus haute que celles dont nous avons besoin, avec une exactitude de 1/10.000^e dans toute l'échelle.

Des piézomètres [2]) avaient été construits pour la détermination précise des isothermes, et l'amélioration et la disposition des cryostats (également avec le souci d'une distribution égale de température dans le bain et de l'invariabilité de celle-ci) est en progrès régulier depuis des années. L'un des thermomètres étalons à hydrogène, qui ont été employés en ces dernières années pour tout le travail de thermométrie du laboratoire aux très basses températures, pouvait donner des références fondamentales en ce qui concerne la thermométrie. Le thermomètre à hélium, qui venait juste d'être comparé au thermomètre à hydrogène, en même temps que le thermomètre étalon auxiliaire de platine, donnait une nouvelle certitude aux déterminations de températures [3]).

Tous ces appareils et les méthodes qu'ils comportent avaient déjà été expérimentés dans un certain nombre de recherches où une précision extraordinairement élevée, de 1 ou 2/10.000^e étaient exigées. En fait, pour des raisons théoriques [4]), le travail sur l'équation d'état au laboratoire avait été dirigé vers l'exploration du domaine où deux ou trois coefficients viriels viennent spécialement en compte pour représenter l'équation d'état. Le domaine des recherches sur l'ammoniaque et le chlorure de méthyle, limité comme il est indiqué ci-dessus où trois coefficients viriels comprenant le premier, donné par les lois des gaz, sont suffisants pour fournir l'équation d'état avec la précision obtenue pour la vapeur d'eau (voir § 5), tombe entièrement dans ce plus large domaine de l'état réduit, que les recherches de Leyde ont en vue.

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[1]) H. KAMERLINGH ONNES, Communication de Leyde, No. 44.

[2]) H. KAMERLINGH ONNES, Communication de Leyde, No. 40.

[3]) Une note sur ce sujet sera publiée à bref délai par MM. KAMERLINGH ONNES et HOLST (voir Comm. N^0. 141*a*).

[4]) H. KAMERLINGH ONNES. Supplément aux Communications de Leyde, No. 9, p. 19.

Disposant de tous les appareils qui ont été installés pour ce travail, on pouvait, en ce qui concerne l'équation d'état des vapeurs surchauffées, effectuer le nouveau travail entrepris avec une précision de 1/10.000^e au moins. Dans cette partie du travail M. Holst pût donc obtenir, au lieu de l'approximation $^1/_2$ pour cent, qui avait été acceptée pour les premières expériences d'établissement du diagramme calorifique, la précision qui a été proposée dans le § 2 comme devant être atteinte dans le travail final du programme de notre Commission, c'est-à-dire celle du diagramme calorifique de la vapeur d'eau.

Les coefficients viriels de l'équation d'état en forme de polynome sont obtenus d'après la détermination d'isothermes dans les piézomètres pour des températures au-dessus de 16° C., quand la détermination des deux coefficients est nécessaire, et par la détermination des coefficients de pression dans les thermomètres pour les basses températures, lorsque la détermination expérimentale d'un tel coefficient viriel suffit (voir § 5).

En ce qui concerne les pressions de vapeur, en construisant [1]) l'appareil pour étalonner les basses températures, toutes les circonstances influençant l'exactitude ont été soigneusement étudiées.

Pour la détermination des chaleurs spécifiques, les appareils ordinaires pouvaient être employés.

§ 5. *Nouvelles données expérimentales recherchées.*

Comme les valeurs des différents termes de l'équation d'état en forme de polynôme de la vapeur surchauffée sont approximativement connues (comme ceux de la substance fictive), on peut calculer combien de termes doivent être employés pour déterminer l'équation d'état avec une précision donnée.

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[1]) Kamerlingh Onnes et Braak. Communication de Leyde, No. 107*a*.

Par là nous pouvons trouver comment distribuer les observations que nous avons eues à faire pour en tirer le plus grand profit et quels sont la nature et le nombre d'observations auxquelles il faut encore procéder pour obtenir une précision donnée dans un domaine donné. M. Holst a effectué ces calculs dans la note IV.

Pour la chaleur spécifique, on peut employer les déterminations de Dieterici, entre 0° et 70° C., dont la précision peut être estimée à 1 %, correspondant à une précision de $^{25}/_{10000}{}^{e}$ dans la chaleur latente de vaporisation.

En résumant tous les calculs de M. Holst (voir note IV) on arrive à la conclusion que la précision que nous avons acceptée pour le travail expérimental peut être atteinte quand les déterminations suivantes sont faites:

Pour l'ammoniaque:

1. quatre isothermes, aux températures de 16° C., 20° C., 40° C., 100° C., pour calculer les deux coefficients viriels nécessaires (le deuxième et le troisième),
2. deux déterminations de coefficients de pression à — 20° C. et à — 40° C., pour calculer le second coefficient viriel dans cette région,
3. les pressions de vapeur en quelques points,
4. les chaleurs spécifiques du liquide au-dessous de 0° C., à — 20° C. et à — 40° C.;

Pour le chlorure de méthyle:

1. une isotherme aux environs de 20° C. pour obtenir une certitude au sujet du troisième coefficient viriel,
2. un coefficient de pression pour déterminer le second coefficient viriel à 40° C.,
3. les pressions de vapeur sur toute l'échelle des températures entre — 40° C. et + 40° C.,
4. la chaleur spécifique du liquide sur toute l'échelle des températures entre — 40° et + 40° C.,
5. la chaleur spécifique du gaz à 0° C., 40° C. et 100° C.

La Note V de M. Holst fournit la plus grande partie de ces données.

Du fait que le travail a été limité, ainsi qu'il est exposé dans le § 2, et du fait que nous avons pu bénéficier des avantages expérimentaux, spécifiés au § 4, il a été possible de présenter dès maintenant ces résultats à la Commission préparatoire.

Les diagrammes construits avec ces données seront publiés dans une note ultérieure qui sera soumise à la Commission préparatoire.

COMMUNICATIONS

FROM THE

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BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 144^b.

◆

G. HOLST. Discussion des mesures faites précédemment sur les propriétés thermiques de l'ammoniaque et du chlorure de méthyle.

(*Translated from: Notes on the Work of the Section for physics, chemistry and thermometry of the first international commission of the Association Internationale du Froid, presented at Third International Congress of Refrigeration, Washington-Chicago,* **Sept. 15** *to* **Oct. 1, 1913**).

EDUARD IJDO. — PRINTER — LEIDEN.

G. HOLST. *Discussion des mesures faites précédemment sur les propriétés thermiques de l'ammoniaque et du chlorure de méthyle.*

NOTES ON THE WORK OF THE SECTION FOR PHYSICS, CHEMISTRY AND THERMOMETRY OF THE FIRST INTERNATIONAL COMMISSION OF THE ASSOCIATION INTERNATIONALE DU FROID

presented by

Prof. H. KAMERLINGH ONNES,
President of the Section.

IV.

NOTE

PRÉSENTÉE À LA COMMISSION PRÉPARATOIRE
pour
L'ÉTUDE DES GAZ FACILEMENT LIQUÉFIABLES
par
G. HOLST.

§ 1. *Méthode.*

Les propriétés thermodynamiques d'un gaz peuvent être calculées si on connait son équation d'état et la chaleur spécifique en un point de chaque isotherme. Car l'équation d'état contient sous forme implicite les propriétés de la vapeur saturée. Elle nous permet de calculer la chaleur de vaporisation et la variation de la chaleur spécifique sur une isotherme en sorte qu'on peut déduire la chaleur spécifique du liquide de celle de la vapeur et inversement. A l'aide de l'équation d'état on peut donc comparer toutes les mesures des propriétés thermiques et calorimétriques dans un système cohérent.

Quoique cette méthode soit la plus générale ce n'est pas celle dont nous nous servirons. D'abord une équation d'état qui représente exactement les résultats des expériences est forcément compliquée et puis le calcul des grandeurs saturées offre des difficultés numériques énormes; c'est pour cela, que nous allons d'une part établir une équation plus simple qui représente l'état gazeux aussi bien que possible, et de l'autre étudier séparément les pressions de la vapeur saturée, la densité du liquide et les chaleurs spécifiques du gaz et du liquide [1]).

§ 2. *L'équation d'état.*

Jusqu'à présent aucune des équations d'état fondées sur des théories du mécanisme intérieur des gaz, n'a pu représenter les observations assez bien pour qu'elle soit utilisable pour les calculs numériques Mais quand il s'agit de différentiations, il est nécessaire d'avoir des expressions analytiques pour les résultats des expériences Faute de mieux on est forcé de se contenter de formules empiriques. M. H. Kamerlingh Onnes a fait une étude très détaillée de la forme d'une telle équation. Il a trouvé que les observations sur l'hydrogène, l'oxygène, l'azote, l'éther et l'isopentane peuvent être représentées par un polynôme de la forme:

$$\frac{\mathfrak{p}\,\mathfrak{v}}{K_4} = \mathfrak{t}\left\{1 + \mathfrak{B}\frac{K_4}{\mathfrak{v}} + \mathfrak{C}\,\frac{K_4^{\,2}}{\mathfrak{v}^2} + \mathfrak{D}\,\frac{K_4^{\,4}}{\mathfrak{v}^4} + \mathfrak{E}\frac{K_4^{\,6}}{\mathfrak{v}^6} + \mathfrak{F}\,\frac{K_4^{\,8}}{\mathfrak{v}^8}\right\}, \tag{1}$$

ou $\mathfrak{p}, \mathfrak{v}$ et $\mathfrak{t}$ sont la pression réduite, le volume réduit et la température réduite,

$$K_4 = \frac{RT_k}{p_k\ v_k}, \tag{2}$$

ou R est la constante des gaz, T_k, p_k, v_k la température critique absolue, la pression et le volume critiques d'une molécule-gramme. Les coefficients $\mathfrak{B}$, $\mathfrak{C}$, $\mathfrak{D}$, $\mathfrak{E}$ et $\mathfrak{F}$, appelés coefficients du viriel, sont des fonctions de la température de la forme:

$$\mathfrak{B} = \mathfrak{b}_1 + \frac{\mathfrak{b}_2}{\mathfrak{t}} + \frac{\mathfrak{b}_3}{\mathfrak{t}^2} + \frac{\mathfrak{b}_4}{\mathfrak{t}^4} + \frac{\mathfrak{b}_5}{\mathfrak{t}^6}. \tag{3}$$

La constante K_4 a été introduite pour éliminer le volume critique de la formule, parce qu' une détermination directe et précise de cette grandeur n'est guère possible.

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[1]) Depuis le commencement de cette étude une recherche analogue a été publiée par G. A. Goodenough et W. M. Earl Mosher, Univ. of Illinois Bull. n⁰. 66, 1913.

Les valeurs des coefficients pour un gaz fictif, qui se comporte comme la moyenne des cinq gaz cités, sont réunies dans le tableau I.

TABLEAU I.

	1	2	3	4	5
$10^8\,\mathfrak{b}$	117,796	— 228,038	— 172,891	— 72,765	— 3,1718
$10^4\,\mathfrak{c}$	135,580	— 135,788	295,908	160,949	51,1090
$10^5\,\mathfrak{d}$	66,0235	— 19,9678	— 137,1572	55,8508	— 27,1218
$10^7\,\mathfrak{e}$	— 179,9908	648,5830	— 490,6830	97,9402	4,58195
$10^9\,\mathfrak{f}$	142,3482	— 547,2487	508,5362	— 127,7356	12,21046

Ces nombres ont été obtenus par le procédé suivant. On a calculé d'abord les coefficients du viriel réduits pour chaque isotherme expérimentale de chacun de ces gaz, puis on a calculé des formules représentant ces coefficients en fonction de la température réduite.

Comme cette équation est la moyenne pour cinq gaz et représente très bien leurs propriétés, il est probable qu'elle peut donner, entre les limites de validité de la loi des états correspondants, une bonne approximation pour l'ammoniaque et le chlorure de méthyle.

Voici une liste des valeurs numériques des coefficients du viriel en quelques points de la région des températures réduites qui nous intéresse :

TABLEAU II.

$\mathfrak{t}$	$\mathfrak{B}$	$\mathfrak{C}$	$\mathfrak{D}$	$\mathfrak{E}$	$\mathfrak{F}$
0,500	— $2{,}3970^{-}9$	0,689378	— 0,0136472	$0{,}0_{3}101473$	— $0{,}0_{5}18030$
0,525	— 2,053138	0,551001	— 0,0102974	$0{,}0_{4}78318$	— $0{,}0_{6}15326$
0,550	— 1,778132	0,447215	— $0{,}0_{2}793153$	$0{,}0_{4}61300$	— $0{,}0_{6}12634$
0,575	— 1,555130	0,368093	— $0{,}0_{2}623051$	$0{,}0_{4}48661$	— $0{,}0_{6}10197$
0,600	— 1,371963	0,306858	— $0{,}0_{2}498617$	$0{,}0_{4}39189$	— $0{,}0_{7}8104$
0,650	— 1,091933	0,218584	— $0{,}0_{2}336067$	$0{,}0_{4}26587$	— $0{,}0_{7}4961$
0,700	— 0,890831	0,165025	— $0{,}0_{2}240330$	$0{,}0_{4}19203$	— $0{,}0_{7}2982$
0,800	— 0,627141	0,101610	— $0{,}0_{2}140352$	$0{,}0_{4}12064$	— $0{,}0_{7}1239$
0,900	— 0,465897	0,069150	— $0{,}0_{3}91400$	$0{,}0_{5}9278$	— $0{,}0_{8}959$
1,000	— 0,359070	0,050776	— $0{,}0_{3}62372$	$0{,}0_{5}8043$	— $0{,}0_{7}1189$
1,100	— 0,283885	0,039547	— $0{,}0_{3}42644$	$0{,}0_{5}7359$	— $0{,}0_{7}1523$
1,200	— 0,228452	0,032265	— $0{,}0_{3}28013$	$0{,}0_{5}6852$	— $0{,}0_{7}1805$

Pour discuter les propriétés d'un gaz quelconque à l'aide de l'équation (1) il faut connaître ses grandeurs critiques.

Les résultats de quelques déterminations du point critique se trouvent dans le tableau III. La pression p_k est exprimée en atmosphères internationales de 76 cm. de mercure, la température t_k en degrés centigrades.

TABLEAU III.

AMMONIAQUE.	p_k	t_k
J. Dewar	115.0	130°.0
C. Vincent et J. Chappuis (1)	113	131.0
M. Centnerszwer (1)	—	132.53
A. Jaquerod	109.6	132.3
F. E. C. Scheffer	111.3	132.10
E. Cardoso et Mlle A. Giltay	112.30	132.90
CHLORURE DE MÉTHYLE.		
C Vincent et J. Chappuis (1)	73	141°.5
J. P. Kuenen	65.38	143.0
C. H. Brinkman	65.93	143.12
M. Centnerszwer (2)	—	143.0
G. Baume	65.85	143.2

Je me suis servi des valeurs obtenues par Cardoso et Mlle Giltay et par Brinkman.

Ammoniaque: $t_k = 132°.90$ C. (405°.99 abs.), $p_k = 112.30$ atm.

Chlorure de méthyle: $t_k = 143°.12$ C. (416.21° abs.), $p_k = 65.93$ atm.

J'ai dit plus haut que nous nous proposions de représenter par une équation les propriétés de l'état gazeux seulement, j'ajoute ici une seconde restriction: nous ne chercherons la représentation que pour la région de pressions et de températures employées généralement dans l'industrie c. à. d. des températures entre —40° C. et 100° C., des pressions au dessous de 30 atmosphères pour l'ammoniaque et de 20 atmosphères pour le chlorure de méthyle.

Alors notre équation se simplifie énormément. S'il s'agit de pressions inférieures aux pressions dites on peut négliger les termes en $\mathfrak{D}$, $\mathfrak{C}$ et $\mathfrak{F}$ de sorte que l'équation devient:

$$\frac{\mathfrak{pv}}{K_4} = \mathfrak{t} \left\{ 1 + \mathfrak{B}\frac{K_4}{\mathfrak{v}} + \mathfrak{C}\frac{K_4{}^2}{\mathfrak{v}^2} \right\}.$$

$\mathfrak{p}$, $\mathfrak{v}$ et $\mathfrak{t}$ sont toujours exprimés en grandeurs réduites. Il sera avantageux d'introduire de nouvelles unités, l'atmosphère, le degré centigrade et le volume normal théorique, c'est le volume que le gaz occuperait à 0° C. et sous une atmosphère, si à partir de l'état gazeux parfait il obéissait à la loi de MARIOTTE.

Cette unité a le grand avantage de contenir le même nombre de molécules pour tous les gaz. Le volume normal théorique de la molécule-gramme est toujours 22,412 litres.

A.
$$pv = RT \left\{ 1 + \frac{B}{v} + \frac{C}{v^2} \right\},$$

ou

$$B = \frac{RT_k}{p_k}\,\mathfrak{B} \qquad C = \frac{R^2 T^2_k}{p^2_k}\,\mathfrak{C}. \qquad R = \frac{1}{273.09}$$

Si nos deux gaz se comportaient conformément à l'équation moyenne, les valeurs de B et C aux différentes températures seraient:

TABLEAU IV.

t	$B \,.\, 10^4$ NH_3	$C \,.\, 10^6$ NH_3	$B \,.\, 10^4$ CH_3Cl.	$C \,.\, 10^6$ CH_3Cl.
— 40°C.	— 207	65.0	— 388	220
— 30	— 183	54.4	— 344	185
— 20	— 164	46.3	— 305	175
— 10	— 147	38.9	— 273	132
0	— 132	33.5	— 247	112
10	— 119	29.3	— 224	98,2
20	— 109	25.8	— 203	86,5
30	— 100	23.0	— 185	76,4
40	— 91	20.4	— 170	67,8
60	— 78	16.3	— 144	54,0
80	— 67	13.5	— 125	44,3
100	— 58	11.4	— 109	37,4

Pour la vapeur saturée de l'ammoniaque le terme $\frac{C}{v^2}$ serait environ 0,4 % à 40° C., 0,07 % à 0° C. et 0,004 % à —40° C. Pour le chlorure de méthyle ce terme serait environ une fois et demie plus grande.

Pour discuter les mesures qui se rapportent à l'équation d'état, j'ai admis qu'une équation de la forme **A** puisse représenter ces mesures et j'ai calculé B et C en fonction de la température.

Les calculs se simplifient souvent beaucoup quand on écrit l'équation d'état sous une autre forme:

B. $$pv = RT\left\{1 + \frac{p}{RT}B + \frac{C - B^2}{(RT)^2}p^2 + \frac{2B^3 - 3BC}{(RT)^3}p^3\right\}$$

C. $$\frac{1}{pv}\frac{\partial pv}{\partial p} = \frac{B}{RT} + \frac{2C - 3B^2}{(RT)^2}p.$$

D. $$\frac{p_1 v_1}{p_2 v_2} - 1 = \frac{B}{RT}(p_1 - p_2) - \frac{B^2}{(RT)^2}(p_1 - p_2)\left\{p_2 + \left(1 - \frac{C}{B^2}\right)(p_1 + p_2)\right\}.$$

Il ne faut pas oublier que le terme du troisième degré n'entre pas dans la représentation $pv = f\left(\frac{1}{v}\right)$.

Il n'en est plus ainsi dans l'équation $pv = f(p)$. Dans la région de pressions dans laquelle une fonction du second degré $pv = f\left(\frac{1}{v}\right)$ peut représenter les observations, il faut prendre une équation du troisième degré de la forme $pv = f(p)$.

D'après l'équation moyenne le terme en p^3 serait égal à 0,25 % de pv à 40° C., 1 % à 60° C. et 2 % à 80° C., pour la vapeur d'ammoniaque saturée. Il faut donc préférer la représentation $pv = f\left(\frac{1}{v}\right)$ à $pv = f(p)$.

§ 3. *Les mesures sur l'ammoniaque.*

Dans leur mémoire sur la détermination du poids atomique de quelques corps M.M. Ph. A. Guye et A. Pintza donnent les résultats de leurs mesures du poids du litre normal d'ammoniaque. Ils se servaient de la méthode du ballon et ils trouvaient 0,7708 gr. Cette valeur a été confirmée remarquablement par les recherches de E. P. Perman et J. H. Davies qui trouvaient comme valeur moyenne de leurs expériences 0,77085 gr. le litre.

A. Jaquerod et O. Scheuer ont determiné la compressibilité à 0°. La formule **D** nous permet de déduire la valeur de B de $1 - \frac{p_1 v_1}{p_0 v_0}$, si l'on prend en première approximation la valeur de C de l'équation moyenne. On trouve $B = -0{,}0149$ et il en résulte 1,3172 litre pour le volume normal théorique d'un gramme.

Cette valeur diffère de 0,1 % du chiffre 1,3160 déduit des poids atomiques. Dans la seconde partie j'ai poursuivi qualitativement la cause de cette différence mais je n'ai pas réussi à la corriger quantitativement. Seulement la valeur 1,3172 est en meilleur accord avec les pesées du ballon de Perman et Davies à quelques autres températures. Dans le tableau V la troisième colonne contient les valeurs de *B* calculées avec la valeur 1,3172, la quatrième avec 1,3160. Les résultats de mesures à 50° et 100° C. m'ont conduit à donner la préférence à la valeur 1,3172.

TABLEAU V.

t	Litre par gramme	*B*	*B'*
— 20° C.	1,19575	— 0,0186	— 0.0177
50	1,5473	— 0083	— 0073
100	1,7964	— 0024	— 0010

On a encore déterminé la compressibilité à quelques températures plus élevées. Tous ces déterminations sauf celle de Regnault se placent fort bien sur une courbe continue.

TABLEAU VI.

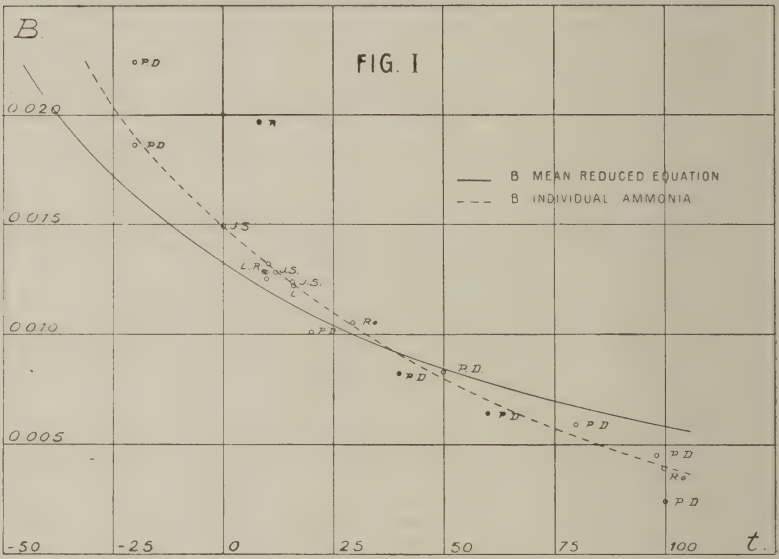
	t	*B*
V. Regnault (1)	8°.1 C.	— 0,0197
A. Leduc	16°	— 0,0122
Lord Rayleigh	10.3	— 0,0132
—	9.2	— 0,0128
—	9.6	— 0,0128
—	9.8	— 0,0125
A. Jaquerod et . . .	11.91	— 0.0128
O. Scheuer . . .	15.71	— 0,0124

Une autre série de valeurs de *B* peut être déduite des mesures du coefficient de compressibilité de l'ammoniaque de Perman et Davies.

t	*B*
— 20	— 0,0225
20	— 0101
40	— 0082
60	— 0064
80	— 0059
98.1	— 0045

Ces valeurs ne correspondent pas très bien avec celles obtenues par la méthode du ballon (tableau V). Mais ces mesures sous faibles pressions ne sont pas très appropriées à la détermination de B. Dans la figure I sont représentées les valeurs individuelles de B calculées d'après les expériences et la courbe $B = f\ (t)$ d'après l'équation d'état moyenne. Elle contient encore deux points $B = -0{,}0105$ à 29°,5 C. et $B = -0{,}0039$ à 99°.6 C. déduites des isothermes de F. Roth.

FIG. I



M. C. Dieterici et H. Drewes ont déterminé le volume spécifique de la vapeur saturée entre 0 et 100° C.

Aux pressions inférieures à 40 atm. on pourrait utiliser leurs mesures pour calculer C à l'aide de la valeur de B de la courbe par les points des autres observateurs. Mais malheureusement aux températures au dessus de 20° C. B n'est pas connu assez exactement.

Il en résulte la nécessité de la détermination de quelques isothermes pour calculer B et C. On voit qu'aux températures au dessous de zéro une détermination de B suffira, C ne jouant qu'un rôle secondaire.

§ 4. *Le chlorure de méthyle.*

Au dessus de 70° C. on possède deux séries complètes d'isothermes déterminées par J. P KUENEN et C. H. BRINKMAN. Une étude comparative des résultats de ces deux physiciens montre que le chlorure de méthyle étudié par BRINKMAN était presqu' absolument pur; d'autre part il y a des irrégularités dans les valeurs de pv de BRINKMAN, qui ne se trouvent pas chez KUENEN. Dans le tableau suivant sont contenues les valeurs approximatives de B déduites de leurs isothermes

TABLEAU VII.

t	B_B	B_K
70° C.	— 0,0116	— 0,0131
85	— 0,0110	— 0,0121
100	— 0,0102	— 0,0110
115	— 0,0094	— 0,0098

On peut remarquer qu'il y a une différence systématique entre les deux séries

A. LEDUC, H. KAMERLINGH ONNES et C. ZAKRZEWSKI, G. BAUME, ont déterminé la compressibilité à 16° C., 20° C. et 0° C. resp.

TABLEAU VIII.

	t	B
LEDUC	16° C.	— 0,0206
K. O. et Z.	20	— 0,0185
BAUME.	0	— 0,0212

Les résultats de KAMERLINGH ONNES et ZAKRZEWSKI concordent avec ceux de BRINKMAN, tandis que le point obtenu par LEDUC se trouve sur la courbe, qui passe par les points de KUËNEN.

BAUME a trouvé pour le poids du litre normal 2,3045 grammes.

Le volume théorique normal d'un gramme calculé à partir des observations de Baume est égal à 0,44353 Litres, tandis qu'on tire 0,44393 des poids atomiques.

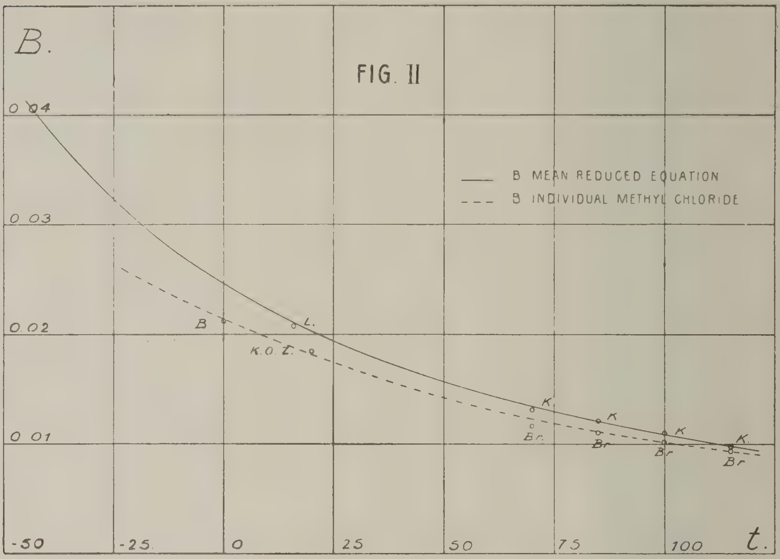


FIG. II

Il sera donc nécessaire de faire quelques nouvelles déterminations pour décider entre les deux séries discordantes et quelques mesures aux températures au dessous de zéro.

§ 5. *La densité du liquide.*

L. Cailletet et E. Mathias ont développé une excellente méthode pour discuter la densité du liquide sous la pression de la vapeur saturée. Quand on trace une courbe qui représente la densité du liquide et de la vapeur saturée en fonction de la température, on voit que les moyennes de ces densités en fonction de la température se trouvent très sensiblement sur une droite, qui passe par le point critique.

Dans le diagramme réduit une seule courbe représenterait les faits si la loi des états correspondants s'appliquait d'une manière rigoureuse.

En réalité on obtient une série de courbes qui s'emboîtent nettement les unes dans les autres.

Nous allons comparer les courbes pour l'ammoniaque et le chlorure de méthyle avec celles de W. **Ramsay** et S. **Young** pour l'éther et de **Young** pour l'isopentane.

La densité critique de l'ammoniaque peut être calculée en partant des mesures de C. **Dieterici** et H. **Drewes**, qui ont déterminé les densités du liquide et de la vapeur à quelques températures entre 0° et 100° C. On en déduit par la méthode du diamètre rectiligne $\rho_k = 0{,}238$.

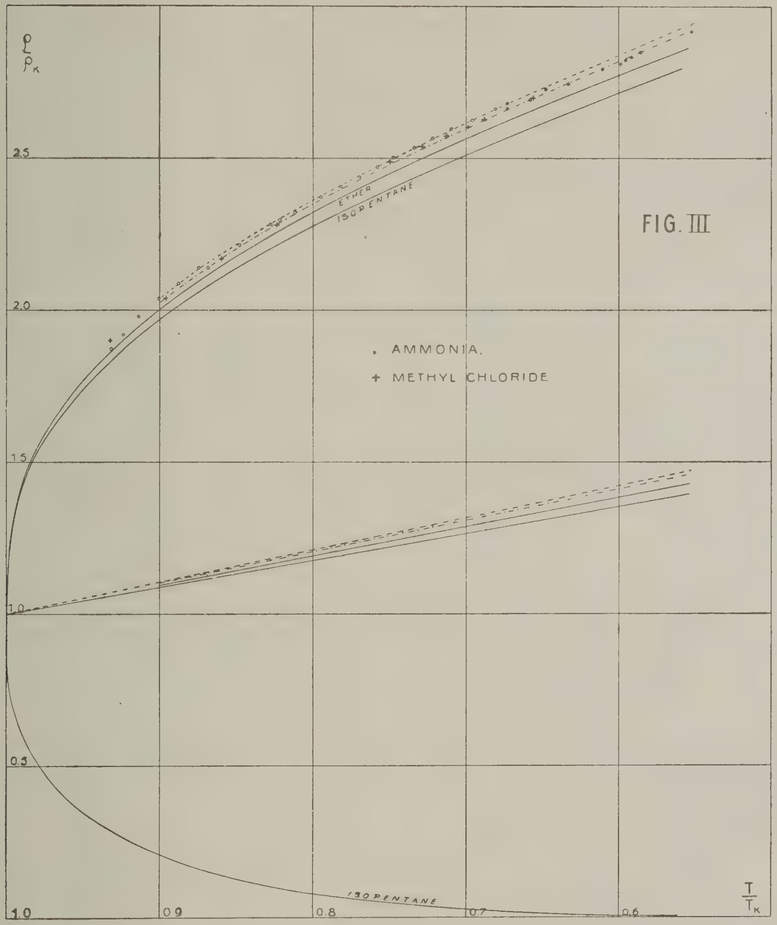


FIG. III

Pour le chlorure de méthyle **Brinkman** trouve par la methode du diamètre $\rho_k = 0{,}353$.

M. Centnerszwer indique $\rho_k = 0{,}370$, tandis que la détermination directe de Kuenen donne une valeur approximative $\rho_k = 0{,}345$.

J'ai dessiné le diagramme des diamètres réduits en me servant des observations de C. Dieterici et A. Lange pour l'ammoniaque, de Kuenen, Brinkman et C. Vincent et Delachanal pour le chlorure de méthyle.

Les mesures des différents expérimentateurs concordent assez bien.

On en peut déduire sans peine les valeurs de la densité du liquide entre + 40° et — 40° C.

Dans la seconde partie je donne les densités du liquide interpolées et extrapolées graphiquement à l'aide de cette courbe. Les valeurs sont probablement exactes à 1 % près, de sorte qu'une nouvelle détermination peut être considérée comme superflue.

§ 6. *La pression de la vapeur saturée.*

Pour discuter les différentes observations sur la tension de la vapeur le diagramme $\log p = f\left(\frac{1}{T}\right)$ est très commode. La courbe est en première approximation une droite qui passe par le point critique:

$$\log \frac{p}{p_k} = f\left(1 - \frac{T_k}{T}\right)$$

ou f est une constante.

Calculant sur la base des observations de Regnault la grandeur f pour la droite, qui passe par le point critique et 0° C. on obtient:

pour l'ammoniaque $f = 2{,}9284$
pour le chlorure de méthyle $f = 2{,}7124$

Dans le tableau IX on trouve les résultats des observations de V. Regnault, A. Blümcke, O. Brill et J. H. Davies sur l'ammoniaque.

Les nombres donnés par R. Pictet sont probablement empruntés à Regnault et non pas le résultat d'une nouvelle détermination.

On voit qu'il y a un écart systématique entre les deux séries d'observations de Regnault aux températures au dessus de zéro. Dans la première série il se servait d'un manomètre ouvert, dans la seconde d'un manomètre fermé à air comprimé. Les déterminations de Blümcke concordent très bien avec les résultats des mesures de Regnault avec le manomètre fermé.

TABLEAU IX.

t.	$p_{\text{obs.}}$	$p_{\text{calc.}}$	$p_{\text{obs.}} - p_{\text{calc.}}$
	Regnault. — Première Série.		
0.—	4.211	4.220	+ 0.001
— 18.03	2.007	2.078	— 0.071
— 16.79	2.125	2.188	— 0.063
— 16.58	2.145	2.207	— 0.062
— 13.09	2.500	2.547	— 0.047
— 12.15	2.607	2.646	— 0.039
+ 3.97	4.758	4.871	— 0.113
+ 4.72	5.016	5.003	+ 0.013
	Regnault. — Seconde Série.		
— 30.96	1.103	1.171	— 0.068
— 31.37	1.084	1.149	— 0.065
— 31.48	1.073	1.143	— 0.070
— 27.36	1.325	1.382	— 0.057
— 27.47	1.320	1.375	— 0.055
— 22.71	1.637	1.700	— 0.063
— 22.60	1.647	1.708	— 0.061
— 18.37	1.998	2.048	— 0.050
— 18.35	1.991	2.050	— 0.059
— 10.42	2.789	2.835	— 0.046
— 10.52	2.808	2.824	— 0.016
0.—	4.216	4.220	— 0.004
0.—	4.220	4.220	0.—
+ 6.93	5.447	5.408	+ 0.039
7.32	5.526	5.482	+ 0.044
7.34	5.524	5.485	+ 0.039
8.45	5.749	5.701	+ 0.048
11.42	6.363	6.310	+ 0.053
13.52	7.020	6.771	+ 0.249
18.15	8.072	7.881	+ 0.191
19.29	8.420	8.175	+ 0.245
19.29	8.399	8.175	+ 0.224
25.35	10.100	9.887	+ 0.213
32.70	12.592	12.325	+ 0.267

t.	$p_{\text{obs.}}$	$p_{\text{calc.}}$	$p_{\text{obs.}} - p_{\text{calc.}}$
	Regnault. — Troisième Série. Manomètre ouvert.		
— 25.70	1.471	1.490	— 0.019
— 25.84	1.443	1.480	— 0.037
— 23.92	1.562	1.612	— 0.050
— 18.31	1.999	2.053	— 0.054
— 18.10	2.013	2.071	— 0.058
— 16.17	2.197	2.245	— 0.048
— 13.15	2.458	2.541	— 0.083
— 13.55	2.447	2.500	— 0.053
— 9.21	2.924	2.974	— 0.050
— 5.03	3.421	3.496	— 0.075
— 0.10	4.157	4.204	— 0.047
+ 6.24	5.216	5.279	— 0.063
	Regnault. — Troisième Série. Manomètre fermé.		
9.98	5.987	6.009	— 0.022
14.38	6.976	6.967	+ 0.009
19.70	8.313	8.283	+ 0.030
30.49	11.583	11.548	+ 0.035
38.90	14.784	14.726	+ 0.059
48.93	19.303	19.353	— 0.050
55.47	22.808	22.922	— 0.114
64.35	28.447	28.541	— 0.094
73.32	35.218	35.211	+ 0.007
81.72	42.330	42.456	— 0.126
	Blümcke.		
— 18.5	1.91	2.04	— 0.13
0	4.22	4.22	0.
34.0	12.80	12.80	0.
63.5	28.04	27.96	+ 0.08
	Brill.		
— 50.7	0.407	0.429	— 0.022
— 46.2	0.531	0.548	— 0.017
— 45.0	0.575	0.584	— 0.009
— 41.5	0.687	0.700	— 0.013
— 39.8	0.748	0.763	— 0.015
— 38.2	0.803	0.827	— 0.024
— 33.0	1.001	1.064	— 0.063
	Davies.		
— 49.8	0.392	0.451	— 0.059
— 41.0	0.699	0.718	— 0.019
— 30.0	1.141	1.225	— 0.084
— 20.0	1.833	1.911	— 0.078
— 15.0	2.271	2.356	— 0.085
— 10.0	2.824	2.883	— 0.059
— 5.0	3.443	3.500	— 0.057

Au dessous de 0° C. il y a de nouveau une petite différence systématique entre les observations de Regnault et Davies et encore entre celles de Davies et Brill.

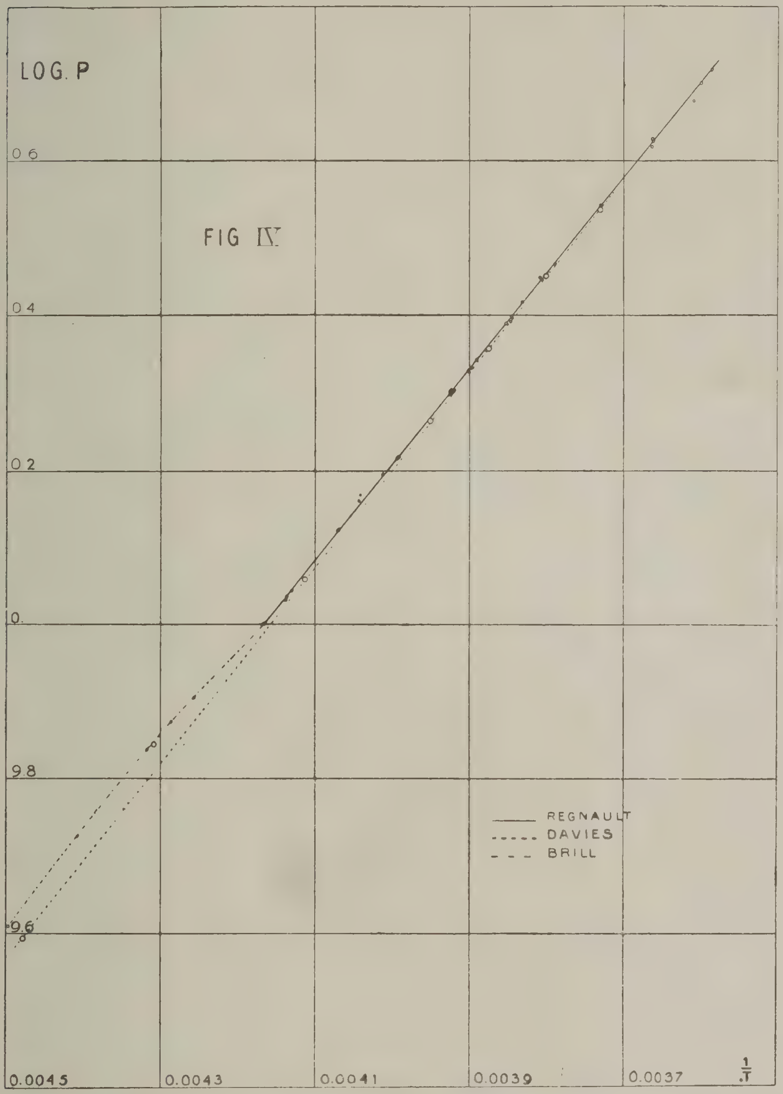


FIG IV

La différence entre Regnault et Davies peut être expliquée par une erreur de 0,2° C. sur la température.

La figure IV représente log p en fonction de $\frac{1}{T}$ au dessous de 0° C.

On voit qu'il sera nécessaire de faire quelques mesures dans cette région des températures à fin de choisir entre les résultats. Aux températures plus élevées il fallait déterminer la tension de la vapeur en quelques points pour décider entre les deux séries de REGNAULT.

V. REGNAULT, C. VINCENT et CHAPPUIS, J. P. KUENEN, C. H. BRINKMAN, CH. M. A. HARTMAN, H. KAMERLINGH ONNES et C. ZAKRZEWSKI ont fait des déterminations de la pression maximale de la vapeur du chlorure de méthyle. Les résultats de leurs observations et leurs différences avec les valeurs calculées d'après la formule de VAN DER WAALS sont consignés au tableau X.

TABLEAU X.

t	$p_{obs.}$	$p_{calc.}$	$p_{calc.}-p_{obs.}$
	VINCENT et CHAPPUIS.		
35	7.50	7.37	— 0.13
40	8.75	8.43	— 0.32
50	11.20	10.91	— 0.31
60	14.30	13.88	— 0.42
70	17.87	17.42	— 0.45
80	22.15	21.60	— 0.55
90	27.65	26.46	— 1.19
100	33.90	32.05	— 1.85
110	41.00	38.44	— 2.56
120	49.80	45.67	— 4.13
130	61.00	53.82	— 7.18
135	65.00	58.26	— 6.74
140	70.60	62.91	— 7.69
141	72.00	63.90	— 8.10

$t.$	$p_{\text{obs.}}$	$p_{\text{calc.}}$	$p_{\text{calc.}} - p_{\text{obs.}}$
		REGNAULT.	
— 29.70	0.771	0.782	+ 0.011
— 26.77	0.873	0.888	+ 0.015
— 24.84	0.951	0.964	+ 0.013
— 22.95	1.033	1.043	+ 0.010
— 21.78	1.084	1.095	+ 0.011
— 19.51	1.188	1.201	+ 0.013
— 14.29	1.479	1.477	— 0.002
— 11.12	1.665	1.668	+ 0.003
— 8.02	1.867	1.873	+ 0.006
— 4.39	2.124	2 138	+ 0.014
0.—	2.498	2.498	— 0.—
4.56	2.942	2.921	— 0 021
10.78	3.609	3.586	— 0.023
16.59	4.288	4.308	+ 0.020
23.03	5.221	5.237	+ 0.016
30.53	6.659	6.505	— 0.154
34.80	7 439	7.325	— 0.114
		BRINKMAN.	
70.12	16.84	17.46	+ 0.62
85.16	22 49	24.00	+ 1.51
100.02	31.44	32.04	+ 0.60
114.96	41.17	41.90	+ 0.73
130.82	53.15	54.51	+ 1.36
		KUENEN.	
69.95	16.59	17.40	+ 0.81
84.95	22.20	23 90	+ 1.70
99.99	30.61	32.03	+ 1.42
115.02	40.46	41.95	+ 1.49
130.10	52.60	53.89	+ 1.29
		HARTMAN.	
9.5	3.48	3.44	— 0.04
		KAMERLINGH ONNES et ZAKRZEWSKI.	
— 25.0	0.959	0.957	— 0.002
— 37.4	0.562	0.552	— 0.010

À l'exception des résultats obtenus par Vincent et Chappuis la concordance est satisfaisante. Malheureusement Regnault se servait d'un thermomètre à mercure dont il n'avait déterminé les corrections qu'aux températures supérieures à 100° C. Cette correction peut atteindre à 0,3° à —30° C. Mais elle est très incertaine. J'ai donc préféré faire quelques nouvelles déterminations que l'on trouvera dans la seconde partie.

§ 7. *La chaleur de vaporisation.*

Dans son mémoire de 1871 sauvé des ruines de son laboratoire Regnault a publié les résultats de 12 déterminations de la chaleur de vaporisation de l'ammoniaque. Il ne donne pas cette grandeur elle même mais une quantité dont on peut la tirer quand on connait la chaleur spécifique du liquide. Maintenant que Dieterici a déterminé cette dernière quantité on peut utiliser les résultats de Regnault.

TABLEAU XI.

t.	λ Regnault.	Corr.	λ Corr.
10.90	292.5	1.7	294.2
15.53	291.5	1.0	292.5
16.00	297.4	1.0	298.4
12.94	289.6	1.8	291.4
11.90	289.9	2.5	292.4
10.72	288.2	6.6	294.8
11.04	291.3	4.6	295.9
10.15	288.4	7.4	295.8
9.52	293.7	6.5	300.2
10.99	294.7	4.4	299.1
12.60	291.6	5.4	297.0
7.80	294.2	2.9	297.1

Les observations ne sont pas assez exactes pour donner λ en fonction de la température mais la valeur moyenne 295,7 cal. à 11°.67 ne peut pas être très éloignée de la vérité.

H. von Strombeck, E. C. Franklin et C. A. Kraus, T. Estreicher et A. Schnerr ont aussi fait des mesures directes de la chaleur de vaporisation.

TABLEAU XII.

	t.	λ
v. STROMBECK	17.°C.	296.5
FRANKLIN et KRAUS . . .	— 33°.4	341
ESTREICHER et SCHNERR . .	— 33°.4	321.3

D'autres auteurs ont calculé la chaleur de vaporisation à l'aide de la formule de CLAPEYRON. Nous procéderons de la même manière. On trouvera les résultats de ces calculs dans la seconde partie.

Une seule détermination directe de la chaleur de vaporisation du chlorure de méthyle à 0° C. a été faite par J. CHAPPUIS au moyen du calorimètre de Bunsen. Il a trouvé $\lambda = 96.9$ cal.

Nous calculerons cette grandeur à partir de nos observations.

§ 8. *La chaleur spécifique du liquide.*

Une étude systématique de la chaleur spécifique de l'ammoniaque liquide en fonction de la température a été entreprise par C. DIETERICI et H. DREWES. Entre 0° et 70° leurs résultats expérimentaux peuvent se représenter par l'équation:

$$C_l = 1,118 + 0.00208\, t.$$

C. LUDEKING et J. E. STARR, L. A. ELLEAU et W. D. ENNIS trouvaient des valeurs plus petites tandis que les observations de H. v. STROMBECK concordent très bien avec celles de DIETERICI.

TABLEAU XIII.

	t.	*C.*
LUDEKING et STARR	0 — 16	0.878
	26 — 46	0.894
ELLEAU et ENNIS	10	1.021
v. STROMBECK	33 — 62	1.229

Au dessous de 0° C. les observations font défaut de sorte qu'il est nécessaire d'y faire quelques mesures.

Pour le chlorure de méthyle, la chaleur spécifique du liquide n'a pas encore été mesurée.

§ 9. *Chaleur spécifique de la vapeur.*

W. Nernst a discuté récemment les mesures de la chaleur spécifique du gaz ammoniaque.

La formule suivante contient les résultats de ses propres mesures combinées avec celles de Voller, F. Keutel, V. Regnault et E. Wiedemann:

$$C_p^{(p=0)} = 0{,}506 + 0{,}000117 + 0{,}423 \frac{t^3}{10^9}.$$

La plus grande différence entre les valeurs observées et calculées est inférieure à 3 %.

Dans la thèse de Keutel on trouve encore une discussion des mesures antérieures de A. Cazin, A. Wüllner et P. A. Müller. Les résultats de Wüllner s'accordent très bien avec la formule de Nernst.

On peut déduire encore la chaleur spécifique des mesures de Wobsa sur l'effet Joule-Kelvin. Je me propose de revenir sur ces mesures dans la seconde partie.

P. A. Müller et J. W. Capstick ont mesuré le rapport des chaleurs spécifiques du chlorure de méthyle.

Müller $\varkappa = 1.199$
Capstick $\varkappa = 1.219.$

La valeur de Capstick est préférable à l'autre (Voir Keutel).

Il est donc nécessaire de faire une détermination de la chaleur spécifique en fonction de la température.

§ 10. *Résumé.*

Cette étude critique nous a donc démontré la nécessité d'une série de mesures nouvelles ayant trait aux points suivants.

Pour l'ammoniaque:

1. Quelques isothermes entre 20° et 100° C.

2. Une détermination pour connaître *B* aux températures au dessous de 0° C.
3. La pression de la vapeur en quelques points.
4. La chaleur spécifique du liquide entre —40° et 0° C.

Pour le chlorure de méthyle:

1. Une isotherme à 20° C.
2. Une détermination de *B* au dessous de 0° C.
3. Les pressions de la vapeur entre —40° et + 40° C.
4. La chaleur spécifique du liquide.
5. La chaleur spécifique du gaz.

J'ai exécuté ce programme sauf ce qui concerne les chaleurs spécifiques (voir à ce sujet Comm. N⁰. 144*d*, page 61).

BIBLIOGRAPHIE.

Pour la bibliographie voir Comm. N⁰. 144*d*.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 144^c.

G. HOLST. Nouvelles recherches sur les propriétés thermiques de l'ammoniaque et du chlorure de méthyle.

(*Translated from: Notes on the Work of the Section for physics, chemistry and thermometry of the first international commission of the Association Internationale du Froid, presented at Third International Congress of Refrigeration, Washington-Chicago,* **Sept. 15** *to* **Oct. 1, 1913**).

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G. HOLST. *Nouvelles recherches sur les propriétés thermiques de l'ammoniaque et du chlorure de méthyle.*

NOTES ON THE WORK OF THE SECTION FOR PHYSICS, CHEMISTRY AND THERMOMETRY OF THE FIRST INTERNATIONAL COMMISSION OF THE ASSOCIATION INTERNATIONALE DU FROID.

presented by

Prof. H. KAMERLINGH ONNES,
President of the Section.

V.

NOTE[1]

PRÉSENTÉE À LA COMMISSION PRÉPARATOIRE
pour
L'ÉTUDE DES GAZ FACILEMENT LIQUÉFIABLES
par
G. HOLST.

§ 1. *Introduction.*

Comme résultat de la discussion précédente nous avons pu délimiter avec assez de précision les expériences qu'il faut faire pour compléter les observations antérieures. Si nous voulons nous borner à la recherche thermique, il faut remarquer, qu'il n'est guère possible d'employer les mêmes instruments pour les mesures à température ordinaire et à basse température. D'abord la température de congélation du mercure constitue une limite inférieure pour l'emploi des piézomètres ordinaires, et puis surtout la construction des cryostats à liquide bouillant offre de grandes difficultés. C'est pour cela que j'ai employé une autre groupe d'instruments pour les mesures au dessous de zéro que pour les mesures à température ordinaire. Mais avant de décrire ces expériences, je vais exposer brièvement la méthode de préparation des gaz.

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[1] Le texte a été amplifié par quelques détails empruntées de la Thèse: G. HOLST, Les propriétés thermiques de l'ammoniaque et du chlorure de méthyle, Zürich 1914.

§ 2. *La préparation des gaz.*

Dans leur travail sur le poids du litre normal de quelques gaz Ph. A. Guye et A. Pintza donnent toutes les indications nécessaires pour préparer de l'ammoniaque pure. E. P. Perman et J. H. Davies, qui ont fait une étude analogue ont employé le même procédé concurremment avec d'autres. Un examen spectroscopique montrait l'absence de toutes bases organiques. La vapeur d'ammoniaque parcourt d'abord un tube de verre dur rempli de chaux vive, chauffée au rouge dans un four à gaz, pour détruire les impuretés organiques. Puis elle est dirigée à travers une solution saturée de potasse caustique pour retenir l'anhydride carbonique et elle est séchée provisoirement sur une colonne de potasse caustique et de baryte anhydre. L'ammoniaque condensée dans un tube refroidi par l'air liquide, le vide fut fait avec une pompe rotatoire à mercure de Gaede pour éloigner les gaz permanents. Elle fut distillée six fois encore et mise en contact avec du sodium métallique ¹) pour retenir les derniers traces d'humidité. En outre la première et la dernière fraction ont été chaque fois rejetées pour obtenir une ammoniaque aussi pure que possible. C'est l'ammoniaque ainsi traitée qui a servi au remplissage des appareils.

Une quantité suffisante du chlorure de méthyle employé par C. H. Brinkman, a été mise à ma disposition. Je tiens à remercier ici M. le Prof. P. Zeeman pour l'amabilité avec laquelle il a bien voulu me céder une provision de ce gaz précieux Ce chlorure de méthyle avait été préparé en chauffant à 80° C. une solution d'anhydride chlorhydrique dans de l'alcool méthylique pur, saturé à 0°, dans un tube de verre fermé. A 80° C. la réaction a lieu et le chlorure de méthyle dégagé est condensé dans une vingtaine de petites ampoules de verre, après un lavage abondant dans l'eau distillée suivi d'un passage par une solution d'anhydride phosphori-

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¹) Voir G. Baume et F. L. Perrot. CR (155), 461, 1912.

que dans l'acide sulfurique concentré pour retenir toute humidité.

Ces petites ampoules furent ouvertes dans le vide. Le chlorure de méthyle fut distillé quelques fois en rejetant la fraction de tête et de queue. Puis il fut employé pour emplir les appareils.

La disposition pour la distillation des gaz était la même que celle employée par G. BAUME dans sa recherche sur le poids du litre normal.

§ 3. *Les piézomètres.*

Pour la détermination des isothermes j'ai employé deux tubes piézomètres de précision du modèle de M. H. KAMERLINGH ONNES, calibrés très soigneusement par M. J. C. SCHALKWIJK.

Après une dizaine d'années le volume n'a accusé aucun changement appréciable, la nouvelle calibration diffère de moins de $^1/_{20000}$ de la calibration antérieure.

Les piézomètres avaient été lavés à l'acide azotique concentré, avec une solution aqueuse de potasse caustique et de l'eau destillée. Je me suis donné la plus grande peine pour bien sécher les tubes. La vapeur d'eau aspirée par une pompe de Gaede était condensée dans un tube immergé dans l'air liquide contenu dans un verre Dewar. Pendant le jeu de la pompe le piézomètre était chauffé avec un brûleur de Bunsen. Le piézomètre est resté pendant quelques jours en connection soit avec la pompe de Gaede soit avec un tube à charbon dans l'air liquide. Après ces précautions je n'ai pu observer aucune absorption appréciable.

Les piézomètres furent remplis à une atmosphère. Pour déterminer la quantité de gaz qu'ils contenaient, je les plaçai dans un bain d'eau à température constante d'environ 20° C. On pouvait déterminer exactement la pression, la température et le volume du gaz. Le second coefficient du viriel étant connu par les recherches antérieures, on peut calculer le volume normal théorique de cette quantité de gaz. C'est ce volume que nous avons choisi comme unité pour exprimer les volumes mesurés. Après la détermination du volume normal les réservoirs des tubes furent placés dans les tubes de compression. Ce sont des tubes du type Cailletet, remplis de mercure.

Les tubes étaient entourés d'un bain d'eau de température constante, muni d'un agitateur.

L'eau circulait dans un système fermé. Sa température était maintenue constante au moyen d'un brûleur à gaz muni d'un régulateur sensible. Les variations de température n'ont jamais dépassé $\frac{1}{40}$° C. Pour obtenir des températures au dessous de la température ambiante, on faisait circuler l'eau dans un serpentin entouré de glace. La circulation était forte, elle se montait à cinq ou six litres par minute. De cette manière j'ai pu réaliser sans peine des températures entre 10 et 50° C.

La température fut déterminée avec deux thermomètres dont l'un, divisé en $\frac{1}{50}$° de degrés, avait été étalonné à la Reichsanstalt. Pour la température de 100° C. j'ai employé le chauffage à vapeur. Un tube rempli d'huile de vaseline muni d'un agitateur était placé à l'intérieur d'un tube plus large dans lequel de la vapeur d'eau était introduite à deux hauteurs différentes. Celle-ci en se condensant chauffait l'huile à 100°. Avant de faire des lectures on pouvait éloigner par un dispositif spécial les gouttes d'eau condensées sur les parois des deux tubes.

La température était controlée avec un petit thermomètre d'Anschütz attaché à l'agitateur.

§ 4. *Le manomètre.*

Pour déterminer la pression du gaz j'ai employé le grand manomètre ouvert, construit par M. H. Kamerlingh Onnes. Il consiste en un système de tubes de trois mètres de longueur qui peuvent être couplés en série. Il permet de lire directement des pressions jusqu' à 60 atmosphères avec une précision de quelques millimètres de mercure. Comme je n'avais pas besoin de pressions audessus de 20 atmosphères j'ai séparé les cinq derniers tubes pour les employer isolément. Ainsi simplifié le manomètre est un instrument très commode; la manipulation est assez rapide et sûre pour ne donner lieu à aucun embarras. Pour la détermination des pressions de la vapeur il est nécessaire de régler le manomètre à une pression fixée d'avance. Pour arriver à cela on ferme le robinet du manomètre et on lit la pression dans le piézomètre sur un manomètre auxiliaire de Bourdon. L'équilibre établi, on ferme le robinet du piézomètre. Un petit calcul fait connaître la hauteur à laquelle il faut faire monter le mercure dans le premier tube du manomètre ouvert pour l'ajuster à la pression du piézomètre.

Après l'ajustage du manomètre on rétablit la communication entre le piézomètre et le manomètre.

§ 5. *Les isothermes.*

Au moyen des instruments, dont je viens de donner la description, j'ai déterminé les isothermes de l'ammoniaque de 19°.5, 24°, 45° et 100°. Pendant le calcul des résultats j'ai trouvé que l'isotherme de 45° accusait un écart assez fort par rapport aux autres. Je ne puis pas me rendre compte de la cause de cette erreur. Il est possible qu'une partie de l'ammoniaque se soit condensée dans la partie inférieure du tube, de sorte que j'ai fait les mesures sur une quantité trop petite d'ammoniaque. Heureusement, j'avais fait une détermination isolée à 39°.5. Elle a pu servir à rectifier cette erreur.

TABLEAU I.

Ammoniaque. Piézomètre IA. V_{thn} = 157.91 ccm.

t.	*p*.	*v*.	*pv*.	*pv—RT*.
24.08	3.783^5	0.27577	1.0434	— 0.0448
24.13	3.772^3	0.27674	1.0439	— 0.0445
24.18	6.599^6	0.15243	1.0060	— 0.0825
24.23	5.710^8	0.17844	1.0190	— 0.0697
19.59	3.619^1	0.28360	1.0264	— 0.0453
19.59	5.531^5	0.18067	0.9994	— 0.0723
Ammoniaque. Piézomètre IIA. V_{thn} = 132.15 ccm.				
39.54	11.260	0.09018	1.0154	— 0.1294
44.92	9.672^7	0.11126	1.0762	— 0.0883
45.03	13.400	0.076920	1.0307	— 0.1342
45.05	17.186	0.05662^5	0.9732	— 0.1918
100.18	10.177	0.12950^5	1.3179	— 0.0489
100.18	13.734	0.09396^2	1.2905	— 0.0763
100.18	21.170	0.05838^1	1.2359	— 0.1309

Pour trouver les coefficients du viriel B et C j'ai calculé

$$\frac{v}{RT}\left(pv - RT\right) = B + \frac{C}{v}.$$

Errata Communication N^{0}. 144*c*.

p. 43 Table III for *t*:	2059	read	20.59
	2058		20.58
	2058		20.58

La représentation graphique montre qu'en prenant $\frac{1}{v}$ comme abcisses et $\frac{v}{RT}\left(pv - RT\right)$ comme ordonnées on obtient un système de lignes droites. Le segment entre l'origine et le point d'intersection de ces lignes avec l'axe des y donne la valeur de B, la tangente de l'angle de ces lignes avec l'axe des x est égal à C.

TABLEAU II.

Ammoniaque.		
t.	*B.*	*C.*
19.6	— 0.01163	— 0.000100
24.1	— 0.01110	— 0 000064
39.5	— 0.00953	— 0.000057
[45.0]	[— 0.00752]	[— 0.000102]
100.2	— 0.00468	— 0.000053

Les valeurs de B obtenues à 19°.5 et 24° concordent très bien avec celles des autres observateurs.

Pour le chlorure de méthyle j'ai déterminé l'isotherme de 20°.5.

TABLEAU III[1].

Chlorure de méthyle. Piézomètre IA. $V_{thn} = 156.72$ ccm.				
t.	*p.*	*v.*	*pv.*	*pv—RT.*
2059	3.4442	0.29168	1.0046	— 0.0708
2058	3.9657	0.25057	0.9937	— 0.0817
2058	4.5692	0.21478	0.9814	— 0.0940

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[1] Les nombres du Tableau III diffèrent un peu de ceux donnés aux Congrès de Chicago à cause de la récalculation du volume normal theorique.

D'abord j'avais calculé le volume normal théorique en tirant la valeur de B de la courbe qui passe par les points expérimentaux de Brinkman—Baume. Cette opération donne une valeur de B plus grande que celle de la courbe. En recalculant le volume normal théorique avec cette nouvelle valeur de B on obtient à la fin une valeur qui concorde admirablement bien avec les chiffres obtenues par Kuenen et Leduc:

$$B = -0{,}0200. \qquad C = 0{,}00024.$$

Je crois donc cette série d'observations préférable à l'autre. Une extrapolation de B jusqu' à zéro ne peut donner lieu à une erreur grave. Je trouve dès lors $B_0 = -0{,}0240$.

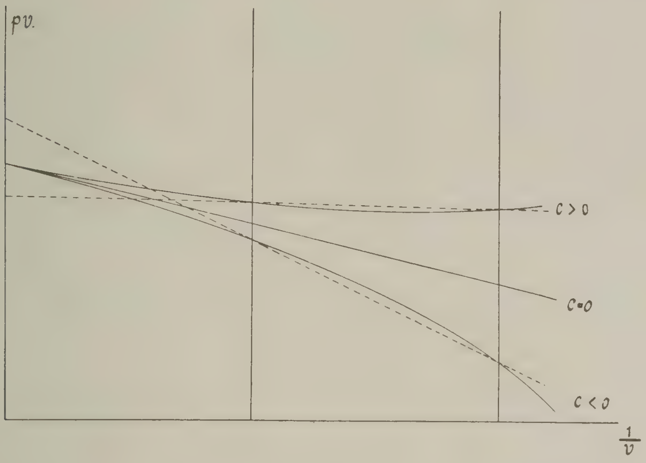
Cette valeur de B_0 et $C_0 = 0{,}0010$ donnent une concordance parfaite entre le volume théorique normal calculé à partir des poids atomiques et le volume théorique normal calculé à partir du volume normal (Baume) et de la compressibilité. Dans le paragraphe suivant je donnerai une description des appareils et méthodes que j'ai employés pour déterminer le coefficient B à des températures au dessous du zéro. Mais je dois tout d'abord attirer l'attention sur la grandeur C.

Comme on voit sur le tableau C est négatif pour l'ammoniaque, tandis que pour le chlorure de méthyle et les autres substances normales il est positif.

L'ammoniaque est une substance anormale qui ne se comporte pas comme les gaz simples. On sait que ses molécules forment des complexes comme dans la vapeur d'eau et quelques autres substances associantes et il est bien possible que le signe négatif de C soit une propriété commune à ces substances. En faisant une représentation graphique de C en fonction de la température on trouve que C augmente très rapidement avec l'abaissement de la température Je crois que c'est ici qu'il faut chercher l'explication des écarts trouvés par les chimistes entre le poids moléculaire des gaz facilement liquifiables calculés à partir du poids du litre normal et de la compressibilité et le poids moléculaire déterminé chimiquement.

La figure montre qu'on trouve une valeur trop grande pour Lim $\left(p\,\frac{v}{v_{th}}\right)$ quand $c < 0$ et une valeur trop petite quand

$c > 0$. C'est justement ce que les expériences de Genève ont donné pour l'ammoniaque où $c < 0$ et pour le chlorure de méthyle ou $c > 0$. Mes expériences ne peuvent pas donner une explication quantitative, mais je crois qu'elles montrent bien clairement où il faut chercher la cause de cet écart.



§ 6. *La détermination du second coefficient du viriel au dessous de zéro.*

Quoiqu'on ne connaisse pas la loi de variation de C avec la température et qu'il soit bien probable que cette grandeur augmente très rapidement, il n'est pas nécessaire de tenir compte du terme en C quand il ne s'agit pas de la plus grande précision. C'est pour cela que je me suis contenté de déterminer B. La méthode que j'ai employée est celle du thermomètre à volume constant. Après une série d'expériences avec un thermomètre construit partiellement en verre de Thuringue qui présentait des phénomènes d'absorption j'ai fait construire un nouveau thermomètre en verre d' Jéna 16^{III}. Avec cet instrument je n'ai pu déceler aucune absorption. Le réservoir avait un volume d'environ 200 cm^3., l'espace nuisible était inférieur à 1 °/₀. La pression indiquée par le manomètre se lisait sur un mètre étalon, divisé en $^1/_5$ de mm., au moyen d'un cathétomètre à deux lunettes. Le réservoir se trouvait dans un cryostat, dans lequel un bain de chlorure de méthyle bouillait sous pression constante. Le cryostat contenait à côté du réservoir un thermomètre à résistance de platine et un agitateur.

Le thermomètre à résistance avait été étalonné peu de temps auparavant avec le thermomètre différentiel à hydrogène et à hélium du laboratoire. Ces indications peuvent être considérées comme justes à $^1/_{50}$ de degré près. Pour mesurer la résistance j'ai employé la méthode du galvanomètre différentiel de Kohlrausch. Pendant les mesures la température a été maintenue constante en faisant varier un peu la pression sous laquelle bouillait le bain de chlorure de méthyle. Les plus grandes variations n'ont pas dépassé $^1/_{40}$ de degré.

J'ai calculé B au moyen de la formule suivante:

$$p_0\left\{\frac{1}{1+B_0\frac{p_0}{76}-B_0{}^2\left(\frac{p_0}{76}\right)^2}+\frac{v_n}{V_0}\,\frac{1}{1+\frac{t_n}{273}+B_{t_n}\frac{p_0}{76}}\right\}=$$

$$=p_t\left\{\frac{1+k_1\,t+k_2\,t^2}{1+\frac{t}{273.09}+B_t\frac{p_t}{76}-B_t\frac{p_t}{76}\,\frac{1}{1+\frac{t}{273}}}+\frac{v_n}{V_0}\,\frac{1}{1+\frac{t_n}{273}+B_{t_n}\frac{p_t}{76}}\right\}$$

ou

p_0 et p_t sont les pressions en cm. de mercure à 0° et à $t°$,

V_0 le volume du réservoir à 0° et 76 cm., v_n t_n le volume et la température de l'espace nuisible,

B_0 B_{t_n} B_t le coefficient B à 0, t_n et $t°$ C.,

$k_1\,t+k_2\,t^2$ la dilatation thermique du réservoir,

$k_1 = 23{,}43.10^{-6}$ $k_2 = 0{,}0272.10^{-6}$, suivant les observations de H. Kamerlingh Onnes et J. Clay.

Les valeurs de B_0 et B_{t_n} sont empruntées à Jaquerod et Scheuer et à Kuenen — Leduc extrapolé.

La dilatation élastique du réservoir était assez petite pour ne pas intervenir dans ce calcul.

Dans le tableau suivant je résume les résultats de mes observations. r désigne le terme qui contient le rapport entre l'espace nuisible et le volume du réservoir.

TABLEAU IV.

t.	*p.*	*r.*	*B.*
Ammoniaque.			
0	51.276	0.00859	— 0.0149
— 23,78	46.692	891	— 200
— 30.48	45.409	858	— 219
— 38.83	43.770	829	— 254
Chlorure de méthyle.			
0	35.210	0.00848	— 0.0240
— 23.64	32.126	831	— 295
— 30.37	31.231	821	— 317
— 38.49	30.174	845	— 339

§ 7. *Les tensions de vapeur.*

Dans la première partie j'ai montré la nécessité de faire quelques déterminations de la pression de la vapeur d'ammoniaque pour décider entre les deux séries d'observation de Regnault. J'ai fait ces mesures dans les piézomètres employés pour l'étude des isothermes. J'ai obtenu les résultats suivants:

$$t = 19^\circ.58\,\mathrm{C}. \qquad p = 8.283 \text{ atm.}$$
$$t = 45^\circ.05\,\mathrm{C}. \qquad p = 17.644 \text{ atm.,}$$

deux points qui se trouvent presque exactement sur la courbe de Regnault, déterminée avec le manomètre fermé. Comme les observations de Blümcke coincident aussi avec cette courbe j'ai rejeté l'autre série de mesures de Regnault pour le calcul d'une formule.

J'avais eu l'intention d'appliquer aux nombres de Regnault une correction résultant d'une nouvelle détermination de l'isotherme de l'air qui donne des pressions un peu plus élevées. Je ne l'ai pas fait à cause de l'incertitude de cette correction, qui pourrait aussi bien donner naissance à une nouvelle erreur. A basse température il fallait faire une nouvelle mesure pour établir les pressions de la vapeur au dessous de — 30° C. Là il y avait deux séries d'observations de **Brill** et de **Davies**, qui présentent une différence appréciable.

Pour ces mesures j'ai employé un cryostat analogue à celui destiné au thermomètre à ammoniaque.

Dans cette recherche on a rencontré beaucoup de difficultés imprévues. D'abord j'ai fait usage d'un appareil analogue à celui employé par **Kamerlingh Onnes** et **Braak** pour la détermination des pressions de la vapeur d'oxygène. J'ai obtenu des pressions de 10 °/ₒ plus élevées que celles observées par **Regnault**.

Puis j'ai préparé de nouvelle ammoniaque croyant que cette différence était causée par des impuretés: j'ai trouvé à peu près le même résultat. J'ai préparé de l'ammoniaque d'après une toute autre méthode; sans succès, j'ai en effet continué à trouver des pressions trop élevées. Alors j'ai fait construire un appareil qui consiste en un tube très large, muni d'un agitateur, et relié à un manomètre de très petit volume.

Au moment où l'on faisait jouer l'agitateur, la pression s'abaissait pour devenir constante après peu de temps. Les résultats ainsi obtenus concordent assez bien avec les mesures de **Regnault**.

TABLEAU V.

Ammoniaque.	
t.	*p*.
— 32.57	1.0323
— 37.35	0.8084
— 43.15	0.5917

Pour le chlorure de méthyle je n'ai pas rencontré cet inconvénient. J'ai pu observer les pressions avec l'appareil de la forme de

Kamerlingh Onnes et Braak, et j'ai obtenu à peu près les mêmes valeurs que Regnault.

TABLEAU VI.

Chlorure de méthyle.	
t.	*p.*
— 47.29	0.3173
— 39.28	0.4869
— 30.26	0.7467
— 22.42	1.0442
— 14.39	1.4941
— 9.78	1.6675
— 4.65	2.1536

Les températures audessous de —20° C. étaient obtenues au moyen d'un bain de chlorure de méthyle. Entre —20° et 0° C. j'ai employé un bain de chlorure d'éthyle.

Ce dernier bain donnait une température constante à $^1/_{100}$° C., probablement le chlorure d'éthyle était-il plus pur que le chlorure de méthyle employé. Aussi à quelques températures plus élevées j'ai déterminé la pression de la vapeur du chlorure de méthyle. En général ces mesures s'accordent assez bien avec les résultats de Regnault.

TABLEAU VII.

Chlorure de méthyle.	
t.	*p.*
10.58	3.658
16.20	4.369
20.58	4.992
26.96	5.974
32.77	7.072
33.18	7.118
39.70	8.625

BIBLIOGRAPHIE.

Pour la bibliographie voir Comm. N⁰. 144*d*.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

N°. 144^d.

G. HOLST. Formules et données regardant les équations d'état, les pressions de vapeur, les volumes de la vapeur saturée, et les chaleurs de vaporisation de l'ammoniaque et du chlorure de méthyle.

(Abstracted from: Thesis for the Doctorate, Zürich 1914.).

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G. HOLST. *Formules et données regardant les équations d'état, les pressions de vapeur, les volumes de la vapeur saturée, et les chaleurs de vaporisation de l'ammoniaque et du chlorure de méthyle.*

§ 1. *Introduction.*

Dans la communication précédante j'ai donné les résultats des expériences que j'avais faites pour compléter les données déjà existantes. Je veux traiter maintenant les équations d'état et les formules pour la pression de la vapeur qu'on peut en dériver. A la fin je donne encore les résultats du calcul de la chaleur de vaporisation et du travail extérieur de l'évaporisation.

§ 2. *Equations d'état.*

Nous allons essayer de représenter nos résultats par des équations. Pour cela il faut exprimer B et C en fonction de la température. La comparaison des valeurs individuelles de B avec celles calculées par l'équation moyenne. montre dejà que la forme $B = f(t)$ pour le chlorure de méthyle peut être choisie analogue à celle de l'équation moyenne. Pour l'ammoniaque la forme est autre. L'ammoniaque a une forte constante diélectrique; il en résulte d'après M. P. Debije la présence de doublets électriques. M. Keesom a calculé la constante B pour un gaz dont les molécules sont de forme sphérique avec un doublet électrique placé au centre. Il a trouvé qu'en ce cas B est une fonction de la température qui ne contient que les puissances paires de $\frac{1}{T}$.

Comme la série ne converge que très lentement aux basses températures, et que la correspondance n'est pas exacte, j'ai calculé une formule avec 3 constantes de la forme:

$$B = 0{,}00236 - 0{,}0625 \left(\frac{100}{T}\right)^2 - 0{,}494 \left(\frac{100}{T}\right)^4.$$

Elle représente B assez bien

TABLEAU I.

t	$B_{obs.}$	$B_{calc.}$	$C_{obs.}$	$C_{calc.}$
100.2	— 0.00468	— 0.00467	— 0.000053	— 0.000053
39.5	— 0.00953	— 0.00921	— 0.000057	— 0.000060
24.1	— 0.01110	— 0.01105	— 0.000064	— 0.000077
19.6	— 0.01163	— 0.1167	— 0.000100	— 0.000083
0.	— 0.0149	— 0.0149	—	—
— 23.8	— 0.0200	— 0.0205	—	—
— 30.5	— 0.0219	— 0.0225	—	—
— 38.8	— 0.0254	— 0.0254	—	—

Pour C j'ai choisi une formule analogue.

$$C = -\,259.1\ 10^{-6} + \frac{50.48}{T^2} - \frac{3.0352\ 10^6}{T^4},$$

de sorte que dans les limites indiquées de pressions et de températures notre équation d'état prend la forme:

$$pv = RT\left\{1 + \frac{1}{v}\left(0.00236 - 0.0625\left(\frac{100}{T}\right)^2 - 0.494\left(\frac{100}{T}\right)^4\right)\right.$$

$$\left. + \frac{1}{v^2}\left(-\,259.1\ 10^{-6} + \frac{50.48}{T^2} - \frac{3.0352.10^6}{T^4}\right)\right\}.$$

Avant de donner une équation d'état pour le chlorure de méthyle je donne les résultats des expériences de Kuenen. Les chiffres diffèrent un peu de ceux publiés dans les Archives; la pression du manomètre à air a été recalculée d'après les nouvelles mesures d'Amagat, le volume est exprimé en fonction du volume normal théorique.

TABLEAU II.

Chlorure de méthyle.

t.	p.	v'.	pv'.	$pv'-RT$.
69.9	15.065	0.068044	1.0251	— 0.2309
69.9	15.425	0.066065	1.0190	— 0.2369
69.9	15.76	0.064182	1.0115	— 0.2444
69.9	16.10	0.062496	1.0062	— 0.2498
69.9	16.44	0.060623	0.9966	— 0.2593
70.0	16.61	0.059398	0.9866	— 0.2697
84.95	16.19	0.067378	1.0909	— 0.2202
84.95	16 586	0.065319	1.0834	— 0.2277
84.95	17.09	0.062809	1.0734	— 0.2376
84.95	17.61	0.060565	1.0665	— 0.2445
84.95	18 13	0.058251	1.0561	— 0.2549
84.95	18.74	0.055908	1.0477	— 0.2633
84.95	19 36	0.053555	1.0368	— 0.2742
84.95	19.40	0.053438	1.0367	— 0.2744
84.95	20.00	0.051193	1.0239	— 0.2872
84.95	20.68	0.048870	1.0106	— 0.3004
84.95	21.49	0.046388	0.9969	— 0.3142
84.95	22.24	0.044124	0.9813	— 0.3297
100.05	16.96	0.068270	1.1579	— 0.2084
99 95	17.67	0.065191	1.1519	— 0.2140
99.95	18 26	0.062643	1.1438	— 0.2221
99.95	19.02	0 059614	1.1338	— 0.2321
99.95	19.86	0.056447	1.1210	— 0.2449
99.95	20.76	0.053506	1.1108	— 0.2552
99.95	21.82	0.049967	1.0902	— 0.2757
99.95	23 15	0.046213	1.0698	— 0.2962
99.95	25.14	0.041213	1.0361	— 0.3299
99.95	25.94	0.039399	1.0220	— 0.3439
99.95	26.66	0.037668	1.0112	— 0.3548
99.95	27 55	0.036125	0.9952	— 0.3707
100 0	28.77	0.033782	0.9719	— 0 3941
99.95	30.71	0.030312	0.9309	— 0.4351
115.0	18.26	0.066985	1.2231	— 0.1979
115.0	20 12	0.059643	1.2000	— 0.2211
115.0	21.57	0.054732	1.1805	— 0.2405
115 0	22.99	0.050575	1.1627	— 0.2583
115.05	24.77	0.046065	1.1410	— 0.2802
115.05	26.80	0.041537	1.1131	— 0.3081
115.0	28.99	0 037203	1.0785	— 0.3426
115 05	31.74	0.032675	1.0371	— 0.3842
115.0	33.53	0.028332	0.9499	— 0.4711
115.0	38.30	0.023949	0 9172	— 0.5038
115.0	40.66	0.021312	0.8665	— 0.5545

J'en ai déduit les valeurs de B et C de la même manière que pour l'ammoniaque. Dans le tableau III ces valeurs sont réunies avec les résultats des expériences de Leduc et des miennes.

TABLEAU III.

Chlorure de méthyle.

t.	$B_{obs.}$	$B_{calc.}$	$C_{obs.}$	$C_{calc.}$
115	— 0.00981	— 0.00982	0.000032	0.000035
100	— 0.01068	— 0.01069	0.000032	000032
85	— 0.01184	— 0.01180	0.000034	000035
70	— 0.01320	— 0.01316	0.000048	000047
20.5	— 0.0198	— 0.01981	0.000190	000189
16	— 0.0206	— 0.02062	—	—
0	— 0.0238	— 0.02379	—	—
— 23.6	— 0.0293	— 0.02954	—	—
— 30.5	— 0.0315	— 0.03150	—	—
— 38.5	— 0.0337	— 0.03397	—	0.000789

Après avoir essayé une série de formules j'ai trouvé que la formule:

$$B = 0.05920 - 0.02046\ 10^3 \frac{1}{T} - 0.1082\ 10^{-6}\ T^2$$

donne une représentation satisfaisante. C augmente rapidement quand la température s'abaisse J'ai choisi une formule de la forme:

$$C = 222.4\ 10^{-6} - 1.633 \frac{1}{T} + 304,1. \frac{1}{T^2}$$

Cette formule peut être employée dans le domaine de températures et de pressions considéré plus haut. Elle ne donne pas de bonnes extrapolations; mais j'ai préféré une formule simple avec peu de constantes valable dans une petite région à une autre, de validité moins restreinte, mais plus compliquée.

L'équation d'état prend donc la forme:

$$pv = RT\left\{1 + \frac{1}{v}\left(0{,}05920 - 0{,}02046\ 10^3\,\frac{1}{T} - 0{,}1082\ 10^{-6}\,T^2\right)\right.$$
$$\left. + \frac{1}{v^2}\left(222.4\ 10^{-6} - 1{,}633\,\frac{1}{T} + 304.1\,\frac{1}{T^2}\right)\right\}.$$

§ 3. *Formules pour la tension de la vapeur.*

J'ai calculé des formules pour représenter la tension de la vapeur en fonction de la température. D'abord j'ai essayé une formule simple à deux constantes analogue à celle de VAN DER WAALS. Elle peut être appliquée à la tension de la vapeur du chlorure de méthyle entre —40° et +40° C. Aux températures plus élevées les écarts deviennent de plus en plus importants. Mais comme nous ne voulons considérer la vapeur saturée que dans la région de températures indiquée je me suis contenté de cette simple relation. Le meilleur accord a été obtenu avec la formule:

$$\log\ p = 4.6007 - \frac{1148.0}{T}.$$

A l'aide de cette formule d'interpolation j'ai calculé des valeurs de p qui se trouvent dans le tableau XI.

La tension de la vapeur d'ammoniaque ne peut être représentée par une expression aussi simple. Après avoir essayé sans succès la formule de NERNST, et une formule de la même forme qui contient encore deux termes de plus, j'ai trouvé satisfaisante la formule:

$$\log p = 4{,}627451 - \frac{976{,}558}{T} - \frac{32082{,}93}{T^2} + 2{,}04.10^{-11}\,(T - 223)^4$$

qui donne une bonne représentation de toutes les observations entre —45° C. et le point critique. C'est avec cette formule que j'ai calculé les valeurs du tableau suivant.

TABLEAU IV.

t	p_{NH_3}	$p_{CH_3Cl.}$
— 40	0.7036	0.4738
— 35	0.9117	0.6012
— 30	1.1675	0.7554
— 25	1.4787	0,9402
— 20	1,8538	1.1608
— 15	2.3017	1,4212
— 10	2.8321	1.7265
— 5	3.4554	2.0824
0	4.1825	2,4944
5	5.0247	2.9685
10	5.9944	3.5112
15	7.1037	4.1289
20	8.3661	4.8285
25	9.7946	5,6171
30	11.3984	6.5020
35	13.2071	7.4907
40	15.2196	8.5907

L'unité de pression est l'atmosphère internationale de 76 cm. de mercure sous conditions normales.

§ 4. *Volume de la vapeur saturée.*

La tension de la vapeur saturée étant connue l'équation d'état nous permet de calculer son volume. J'ai employé l'équation d'état de la forme $pv = f(p)$. Le résultat de ce calcul se trouve dans le tableau V qui contient aussi le volume du liquide sous la pression de la vapeur déduite du diagramme des diamètres rectilignes.

TABLEAU V.

t	$v_{\text{vap}}^{NH_3}$	$v_{\text{liq}}^{NH_3}$	$v_{\text{vap}}^{\text{Diet}}$	$v_{\text{vap}}^{CH_3Cl.}$	$v_{\text{liq}}^{CH_3Cl.}$
— 40	1562,6	1.449		784.3	0.976
— 35	1226,6	1.464		629.1	0.983
— 30	973,4	1.477		509.0	0.992
— 25	780,2	1.490		415.5	1.001
— 20	631,2	1.506		341.6	1.010
— 15	515,1	1.520		282.9	1.019
— 10	423,7	1.536		235.9	1.029
— 5	351,2	1.550		198.0	1.038
0	293,1	1.567	294.0	167.1	1.048
5	246,2	1.585	245.5	141.9	1.059
10	208,0	1.603	206.0	121.0	1.071
15	176,8	1.621	174.0	103.8	1 082
20	151,0	1.639	148.0	89.39	1.094
25	129,6	1.658	126.5	77 31	1.106
30	111,7	1.678	108.5	67.13	1.119
35	96,6	1.701	93.2	58.50	1.131
40	83,9	1.721	80.9	51.13	1.144

Dans la quatrième colonne j'ai ajouté les nombres obtenus par C. Dieterici. A zéro degrés la concordance est parfaite, mais les différences augmentent avec la température ascendante et s'élèvent à 4 % à 40° C. Je suis conduit à penser qu'il faut chercher la cause de cet écart dans la possibilité d'une absorption de l'ammoniaque, phénomène que j'avais pu observer dans le thermomètre à ammoniaque en verre de Thüringe. Dans la méthode de Young, employée par Dieterici on ne peut pas déceler ce phenomène et on n'a pas de contrôle qu'une telle absorption n'a pas eu lieu. Mais il peut être aussi que cette différence ait été provoquée par des erreurs dans la courbe des tensions de vapeur. En tout cas les recherches de R. B. Brownlee, H. A. Babcock et F. G. Keyes, dont le rapport provisoire a été présenté au congrès du froid de Chicago de 1913, peuvent nous donner des renseignements sur cette question; mais il faut attendre la publication des résultats définitifs de leurs expériences.

§ 5. *La chaleur de vaporisation.*

J'ai calculé la chaleur de vaporisation de l'ammoniaque et du chlorure de méthyle en me servant de la formule de Clapeyron. Les résultats ainsi obtenus et le travail de vaporisation sont consignés dans le tableau VI

TABLEAU VI.

t	r_{NH_3}	λ_{NH_3}	r_{CH_3Cl}	λ_{CH_3Cl}
— 40	328.5	26.57	101.8	8.98
— 35	325.5	27.02	101.4	9.13
— 30	322.5	27.44	100.9	9.28
— 25	319.3	27.85	100.4	9.43
— 20	316.0	28.23	99.9	9.56
— 15	312.6	28.59	99.2	9.69
— 10	309.0	28.92	98.5	9.81
— 5	305.3	29.22	97.8	9.92
0	301.4	29.49	97.0	10.02
5	297.4	29.73	96.1	10.11
10	293.2	29.93	95.1	10.19
15	288.9	30.09	94.1	10.26
20	284.4	30.22	93.0	10.31
25	279.6	30.30	91.8	10.35
30	274.8	30.34	90.5	10.38
35	269.6	30.32	89.2	10.39
40	264.2	30.26	87.7	10.39

Cela ne nous étonne pas de trouver encore des différences avec les calculs de DIETERICI. Peut être les recherches américaines peuvent elles résoudre définitivement la question.

Pour le chlorure de méthyle au contraire j'ai trouvé une valeur tout à fait identique à celle obtenue par J. CHAPPUIS.

Quoique j'eusse originairement l'intention de terminer cette étude sur les propriétés thermiques de l'ammoniaque par un calcul de la variation de la chaleur spécifique de ce gaz en fonction de la pression et un calcul de l'effet JOULE-KELVIN pour comparer les expériences de WOBSA avec les miennes, je n'ai pas effectué ces calculs. Au congrès de Chicago BROWNLEE, BABCOCK et KEYES ont publié un rapport provisoire sur une étude détaillée de l'ammoniaque. Dans ces circonstances il me semble préférable d'attendre la publication définitive de leurs mesures. Après on pourra employer l'ensemble des nouvelles recherches pour le calcul de nouveaux tableaux.

Quant au chlorure de méthyle mon départ de Leiden m'a empêché d'achever la détermination de ses propriétés calorimétriques. J'avais construit un calorimètre à flux continu d'après CALLENDAR et BARNES muni d'éléments thermoélectriques pour mesurer la chaleur spécifique du liquide. Cette méthode offre le grand avantage qu'on peut travailler sous une pression un peu plus grande que celle de la vapeur saturée de sorte qu'aucune correction pour l'évaporisation du liquide n'intervient dans le résultat. Pour déterminer la chaleur spécifique de la vapeur j'avais construit un calorimètre d'après SCHEEL et HEUSE dans lequel le même principe du flux continu est appliqué. Heureusement on a entamé ces recherches dans un autre laboratoire de sorte que dans peu de temps on pourra disposer d'un tableau complet pour ce gaz.

A la fin de ce travail il m'est un devoir très agréable de remercier M. le Professeur H. KAMERLINGH ONNES pour l'amabilité avec laquelle il a mis à ma disposition tous les moyens de travail nécessaires dans ces recherches. Le temps, pendant lequel j'ai eu l'honneur d'être son assistant et plus spécialement les années pendant lesquelles j'ai eu le plaisir de l'assister dans ses propres recherches, resteront toujours une période de ma vie à laquelle je ne pourrai penser qu'avec un sentiment de vive reconnaissance.

BIBLIOGRAPHIE.

Barnes. H. T. Phil. Trans. (**A** 199), 149, 1902.

Baume. G. Journ. de Chim. Phys. (6), 1, 1908.

Blümcke. A. Wied. Ann. (34), 18, 1888.

Brill. O. Ann. d. Phys. (21), 170, 1906.

Brinkman. C. H. Thèse, Amsterdam.

Brownlee. R. B., H. A. Babcock et F. G. Keyes. Rapport. Congrès du Froid Chicago 1913.

Cailletet L. et E. Mathias. Journ. de Phys. (5), 549, 1886.

Callendar H. L. Phil. Trans. (A 199), 55, 1902.

Capstick. J. W. Proc. Roy. Soc. (54), 101, 1893.

Cardoso M. E. et Mlle A. Giltay. Journ. de Chim. Phys. (10), 514, 1912.

Cazin. A. Ann. d. Chim. (56), 206, 1862.

Centnerszwer. M. 1. Zeitschr. Phys. Chem. (46), 456, 1903.

„ „ 2. „ „ „ (49), 199, 1904.

Chappuis. J. Ann. Chim. Phys. (15), 498, 1888.

Davies. J. H. Proc. Roy. Soc. (78), 41, 1906.

Debije. P. Phys. Zeitschr. (13), 97, 1912.

Dewar. J. Phil. Mag. (18), 210, 1884.

Dieterici. C. Zeitschr. f. d. ges. Kälte Ind. (11), 21, 47, 1904.

Drewes. H. Thèse. Hannover.

Elleau. L. A. et W. D. Ennis. Journ. Frankl. Inst. (145), 189. 280, 1898.

Estreicher. T. et A. Schnerr. Bull. de l'Ac. de Cracovie, p. 345. 1910.

Franklin. C. et C. A. Kraus. Journ. Phys. Chem. (11), 553. 1907.

Guye. Ph. A. et A. Pintza. Mém. de la Soc. de Phys. de Genève. (35), 572, 1905—1907.

Hartman. Ch. M. A. Comm. Leiden. N⁰. 64.

Jaquerod. A. Ber. D. Ch. Ges. (39), 1451, 1906.

Jaquerod et O. Scheuer. Mém. de la Soc. de Phys. de Genève. (35), 659, 1905—1907.

Kamerlingh Onnes. H. Comm. Leiden, N⁰. 71, 74, Suppl. N⁰. 8, p. 6. Suppl. N⁰. 19. p. 17.

Kamerlingh Onnes et C. Braak. Comm. Leiden, N⁰. 107*a*.

Kamerlingh Onnes et J. Clay. Comm. Leiden, N⁰. 95*b*. Voir N⁰. 95*e*. p. 60, note.

Kamerlingh Onnes et W. H. Keesom. Enc. d. math. Wiss. Comm. Leiden. Suppl. N⁰. 23.

Kamerlingh Onnes et C. Zakrzewski. Comm. Leiden. N⁰. 92.

Keesom. W. H. Comm. Leiden. Suppl. N⁰. 24*b*.

Keutel. F. Thèse. Berlin.

Kuenen. J. P. Arch. Néerl. (26), 354, 1898.

Lange. A. Zeitschr. f. d. ges. Kälte Ind. (5), 39, 1898.

Leduc. A. Recherches sur les gaz. 1898.

Lüdeking. C. et J. E. Starr. Phil. mag. (35), 393, 1893.

Müller. P. A. Wied. Ann. (18), 94, 1883.

Nernst. W. Zeitschr. f. Elektrochem. (17), 49, 1910.

Perman. E. P. et J. H. Davies. Proc. Roy. Soc. (78), 28, 1906.

Pictet. R. Nouvelles machines frigoriques. 1885.

Ramsay. W. et S. Young Phil. Trans. (178), 57, 1887.

Rayleigh. Lord. Zeitschr. Phys. Chem. (52), 731, 1905.

Regnault. V. 1. Mém. de l'Ac. (26), 252, 1862.
„ 2. „ (26), 596, 1862.
„ 3. „ (26), 594, 1862.
„ 4. Ann. Chim. Phys. (24), 375, 1871.
„ 5. Mém. de l'Ac. (26), 161, 1862.

Roth. F. Wied. Ann. (11), 1, 1880.

Schalkwijk. J. C. Comm. Leiden, N⁰. 70.

Scheel. K. et W. Heuse. Ann. d. Phys. (37), 79, 1912.

Scheffer. F. E. C. Zeitschr. Phys. Chem. (71), 694, 1910.

Strombeck. H. v. 1. Journ. Frankl. Inst. (131), 7, 1891.
„ 2. Journ. Frankl. Inst. (130), 467, 1890.

Vincent. C. et J. Chappuis. 1. Journ. de Phys. (5), 58, 1886.
„ „ „ 2. C. R. (100), 1216, 1885.

Vincent. C. et Delachanal. Ann. Chim. Phys. (16), 427, 1879.

Voller. F. Thèse. Berlin.

Wiedemann. E. Pogg. Ann. (157), 1. 1876.

Wobsa. G. Thèse. Dresden. Zeitschr. f. d. ges. Kälte. Ind. (14), 61, 1907 et (15) 11, 1908.

Wüllner. A. Wied. Ann. (4), 321. 1878.

Young. S. Proc. Phys. Soc. London (13), 602, 1895.

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UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

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N°. 144.

H. KAMERLINGH ONNES. Organisation des expériences sur les propriétés thermodynamiques de l'ammoniaque et du chlorure de méthyle.

G. HOLST. Discussion des mesures faites précédemment sur les propriétés thermiques de l'ammoniaque et du chlorure de méthyle.

———. Nouvelles recherches sur les propriétés thermiques de l'ammoniaque et du chlorure de méthyle.

———. Formules et données regardant les équations d'état, les pressions de vapeur, les volumes de la vapeur saturée, et les chaleurs de vaporisation de l'ammoniaque et du chlorure de méthyle.

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